Journal of the
OPTICAL SOCIETY
of AMERICA

VOLUME 34, NUMBER 1 JANUARY, 1944

Bright Diffraction Gratings*

HAROLD D. BABCOCK
Mount Wilson Observatory, Carnegie Institution of Washington, Pasadena, California

I. INTRODUCTION

WHEN diffraction gratings of high quality became available about sixty years ago they proved almost ideal for the spectroscopic study of the sun and the electric arc. For the observation of stellar spectra, however, prisms have been almost universally employed because of their greater economy of light. As this situation is now changing, with implications of importance for future observers, it is appropriate to examine the problem of producing brighter gratings and to appraise the results thus far attained.

This paper discusses only the control of the intensity in grating spectra. It necessarily omits the treatment of mechanical errors in ruling machines and related questions. As will be shown, gratings can now be designed and made with such concentration of light in one order that they compare favorably with prisms at either high or low dispersion. Additional improvements, which may be expected after the return of peace, will doubtless make the technique more certain and the grating more permanent, but can further augment the brightness by only minor amounts.

In his book, *The Sun*,[1] Professor C. A. Young remarked ". . . it is possible, by giving the proper shape to the diamond point which rules the lines and properly regulating the depth of cut, to produce gratings in which most of the light shall be concentrated in a single one of the spectra at the expense of the rest."

It seems probable that Young obtained this idea from Rowland, with whom he undoubtedly discussed the construction and use of gratings. From his own remarks[2] it is clear that Rowland utilized only uncut diamonds as ruling tools. Long patient testing of such stones sometimes led to the discovery of one giving exceptional brightness, as indicated in his remark "in the green the reflecting speculum grating may be brighter than a prism spectroscope of five prisms, and for higher dispersion surpasses the prism spectroscope both in definition and brightness in all portions of the spectrum."

Although Rowland saw the possibility of controlling the brightness, it remained for Anderson in 1916 to begin at the Mount Wilson Observatory the practical development of Young's suggestion, through the introduction of two ideas: (1) the artificial shaping of the ruling diamond, and (2) the formation of the grooves, not by cutting or scraping, but by plastic deformation of the metal.

To produce the ruling tool, Anderson and Jacomini constructed a machine of novel design with which two convex conical surfaces are cut

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] C. A. Young, *The Sun* (D. Appleton-Century Company, Inc., New York), 1895 edition, p. 67.

[2] H. A. Rowland, Johns Hopkins University Circulars, No. 17 (1882); *Encyclopaedia Britannica*, "Diffraction gratings" (1902).

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and polished on a diamond. The intersection of these surfaces is the ruling edge, which moves in its own direction across the plate, pressing the grooves to the contour of the diamond and burnishing them at the same time. The ruling edge may for the moment be visualized as somewhat like the keel of a little boat with both bow and stern rising above the surrounding water, i.e., the metal of the grating.

As early as 1924 they produced six-inch and

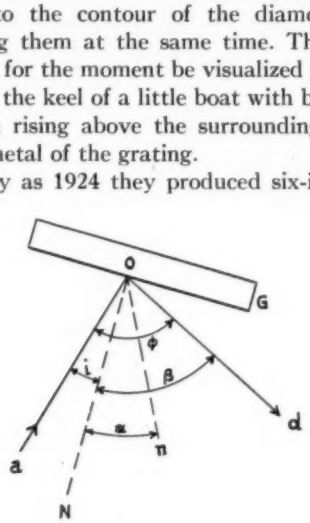

FIG. 1.

four-inch speculum gratings having high concentration of light in one first-order spectrum. These gratings are still in constant use, having required only an application of evaporated aluminium to render them comparable in intrinsic brightness with the best that have since been made here or elsewhere.

Since 1929 I have further developed Anderson's method. With the aid of E. D. Prall the diamond cutting machine has been rebuilt, the art of preparing the diamonds has been advanced, and the control of brightness has been accomplished for both coarse and fine spacings on surfaces of widely different character. So far as I know, other workers are using only diamonds cut with plane sides.

II. THEORY

To concentrate into a given direction the light which leaves a reflection grating, the walls of each groove are made flat, one being as wide as possible and the other narrow. The inclination of the wide side with respect to the surface of the grating is then so chosen that its specularly reflected ray coincides in direction with the desired diffracted light. Obviously, if the reflected component is to be of much value, the width of the wide sides of the grooves must exceed the wave-length of the light that is used. Experience shows that with about 15,000 grooves per inch a valuable control may be had, although coarse rulings having from 500 to 1000 grooves per inch afford a more striking illustration of the principles. With finer spacing such as 45,000 per inch, i.e., about one wave-length for visible light, the distribution of the light is determined mainly by diffraction.

The plane of the diagram in Fig. 1 is perpendicular to the grooves on the face of the reflecting grating G, the normal to whose surface is indicated by N. Arrows show an incident and a diffracted ray related to a single element of the ruling at O. From the law of reflection it is obvious that in order to reflect the incident ray in the same direction as that taken by the diffracted ray, an elementary mirror at O must be perpendicular to n, the bisector of the angle aOd, and must therefore define the angle α with the face of the grating, such that $\alpha=(\beta-i)/2$.

Figure 2 shows schematically the cross section of a few grooves in an idealized grating, with the angle α indicated. It is essential to get as much as possible of each grating space into one side of each groove at the expense of the other, especially in closely spaced rulings.

The design of a ruling which will have a maximum intensity at a given region in its angular field involves nothing more than the determination of that value of α which will cause the incident light to be reflected in the desired direction. Three simultaneous equations express the general relation between the various quantities involved, as well as the special conditions which have been mentioned.

1. $m\lambda=a(\sin i\pm\sin\beta)$
2. $\phi=i\mp\beta$
3. $\alpha=(i\pm\beta)/2$.

Here m=order of spectrum, λ=wave-length of

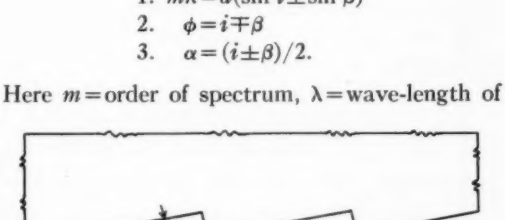

FIG. 2.

light, a=grating space, i=angle of incidence on the grating, β=angle of diffraction, ϕ=angle between axes of collimator and camera, and α=angle between original plane of grating and the wall of a groove. For upper signs throughout, the incident and diffracted rays are on the same side of the normal to the grating, while for lower signs they are on opposite sides. If m, λ, a, and ϕ are specified, α is determined.

In the case of a transmission grating, such as a transparent replica made from a ruled metallic surface, α is the refracting angle of each one of the elementary prisms which form the active surface. The diagram of Fig. 3 represents a cross section perpendicular to the replica and to the prismatic ridges, which are supposed to be perfect casts of the grooves in the original grating. Light incident normally, as indicated, is deviated by refraction through the angle δ according to the relation $n \sin \alpha = \sin(\alpha+\delta)$ where n is the index of refraction of the material forming the replica. For maximum intensity δ must correspond to the direction of the desired diffracted ray, which is determined by $m\lambda = a \sin \delta$, where the symbols have the same meaning as before. The two relations determine α and δ when λ, m, a, and n are given. The original grating is then ruled with the calculated value of α and a replica is made.

III. PRACTICAL APPLICATION AND RESULTS

It might seem that, after preparing a ruling diamond, the only requirements are its correct angular adjustment and sufficient load to cause adjacent grooves to touch. But this last detail, which is essential for saving light that would otherwise appear in the zero order, becomes complicated by the distortion that too often affects a groove when the next one is formed. This effect depends on the type of metal, its manner of preparation, the dimensions of the grooves, and the azimuthal adjustment of the diamond, as well as other factors. The schematic diagram of Fig. 2, though based on the known contour of the diamond, may be only a rough approximation to the real structure of the grating, which must be inferred from its performance or obtained by direct examination under a microscope.

If a full-sized grating is available for testing it is mounted in a spectroscope of 20 feet focal length and its monochromatic (Hg light) images of a very wide slit are visually matched in brightness with those formed by a plane mirror of variable aperture, with the aid of filters. This gives the percentage of incident light present in each order of the spectrum, a more useful datum than the percentage of diffracted light, and makes possible a comparison of the grating with prisms.

Microscopic examination is a valuable independent guide but brings its own difficulties. Every microscopist is familiar with the uncer-

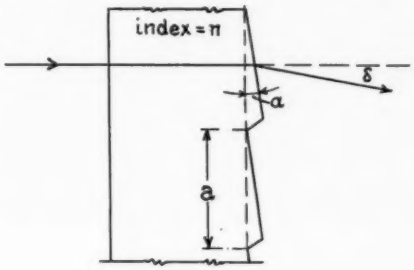

FIG. 3.

tainties of interpreting the appearance of a periodic structure when the limit of resolving power of his instrument is approached. Spurious details, delicately responsive to the slightest variation in the focal adjustment or in the illumination, are particularly troublesome in a field of parallel equidistant lines.

True microscopic perspective in a ruled surface may nevertheless be obtained by ruling a single groove across the grating transverse to the main ruling. Variations in the width of the single groove reveal without ambiguity the relative heights which otherwise are so difficult to determine. Such tests show that, even though the form and position of the diamond may have been correctly determined from the theory, the final shape of the grooves may be appreciably different.

Because of the necessary dissymmetry in the grooves, a choice must be made between two procedures. In one of these the wide side of the groove lies toward unruled metal during the making of the grating, in the other it lies toward that part of the surface which has already been ruled. Under some circumstances it is distinctly valuable to make this discrimination.

The use of gratings for observation of stellar spectra was begun at this Observatory experi-

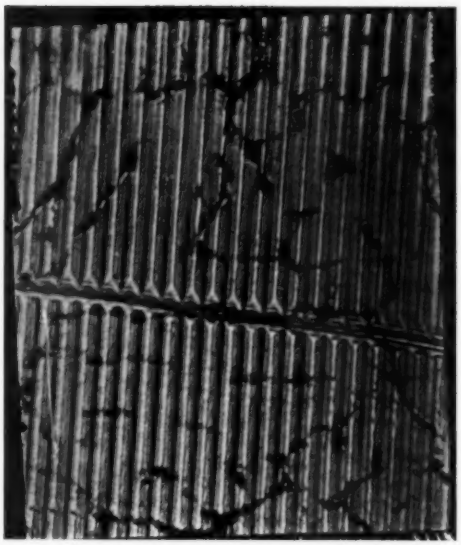

FIG. 4. Photomicrograph of a speculum diffraction grating having very bright second order. Grating space =1/600 mm. Enlargement 1920×. An accidental scratch reveals the perspective of the rulings. Aberrations, especially at the top, illustrate the well-known difficulty of interpretation of such a structure in the absence of a geometrical test such as that given by the scratch. Photographed with 2-mm oil immersion apochromatic objective and ×18 compensating ocular. Vertical illuminator.

FIG. 5. Photomicrograph of a grating ruled on heavy electrolytic film of silver on a rolled copper base. The matte silver was buffed before ruling. Wide side of groove inclined 2° to original plane. Grating space=1/30 mm. Enlargement 312×. For perspective a single groove was ruled across the grating with the same diamond. Curved contour in the cross ruling indicates distortion in wide sides of grooves. Order of progression is from right to left, i.e., steep side of diamond is toward unruled metal. Note imperfect burnish at shallow side of each groove. Oblique illumination through vertical illuminator. 5.5-mm achromatic objective ×10 compensating ocular.

mentally by Adams in 1906. About sixteen years later systematic investigations were undertaken by Merrill, who photographed hundreds of spectra at medium dispersion with gratings ruled in our instrument shop by Anderson and Jacomini. High dispersion spectra of bright stars have been regularly observed with gratings by Adams and his co-workers since 1932, while recently Minkowski has employed gratings of special design for the study of faint objects under very low dispersion. These researches have clearly shown the advantages of gratings over prisms. For example, Minkowski photographed the entire visible spectrum of an *A*-type star with two prisms and again with the grating. The dispersion between H_β and H_δ was the same, as was also the exposure time. The prismatic spectrum is useful from the violet to the green but then through loss of dispersion becomes of little value. The grating spectrum, because of its nearly uniform dispersion, is measurable from violet to deep red, a range about twice as great as that of the prism.

When low linear dispersion is to be obtained with a camera of long focus, as with an objective stellar spectrograph, coarsely spaced transmission gratings offer advantages over prisms. One way of producing such a grating is to make a transparent replica from an original ruling on metal, a method limited by the size of the replica that can be made optically adequate. As is well known, Professor R. W. Wood has met with encouraging success in his attempts to build a large mosaic of individual replicas.

At the Mount Wilson Observatory the problem has been approached from a different direction. Our purpose is to rule a full-sized grating, 18 inches square, and attempt to produce a single replica from this. Although interrupted by the war, our experience has been encouraging and some phases of it will be described and illustrated (see Figs. 4 and 5).

Soft-rolled plates of Cu, Al, and Duralumin, electrolytic films of Ag, Ni, and Cu, hard-rolled plates of Cu, castings of Pb-Sn alloys in several ratios, and evaporated films of Al, Ag, Cu, Au, and Sn on glass have been included in this study. For most of the evaporated films I am indebted to Dr. John Strong, who produced them of the extraordinary thickness of about 5μ, all highly lustrous except Sn, which, however, partially burnished under the diamond.

With diamonds designed for the purpose these metals have been ruled with about 800 grooves per inch so as to produce strong maxima in the yellow of one-fourth order. Replicas of cellulose acetate are intensely bright in the first order and give their theoretical resolving power in the small sizes thus far made. Our experience indicates a rolled aluminium plate as the best material for this type of ruling. On such a surface we have produced grooves most nearly free of distortion and the intensity maximum is correspondingly narrow and high.

Let the intrinsic brightness I be defined as the percentage of the incident monochromatic light which is found in the emergent beam from unit area of a ruled surface. As we have seen, I is readily measured for the green mercury line. My own observations show that with about 600 grooves per mm the brightest rulings made in our laboratory, like those produced by Professor Wood by a different technique, have values of I ranging up to 60 percent. Such brightness is usually provided in a first-order spectrum, but in one ruling we succeeded in attaining it in a second order. For coarser spacing, about 300 grooves per mm, for which we have only our own gratings to study, I has been made as high as 70 percent in the first order. Our brightest replicas from gratings having 30 grooves per mm have 85 percent of the incident light in the first order.

TABLE I.

Spacing mm	Gratings Ang. disp.	I	Prisms $n=1.61$ No.	Angle	Ang. disp.	I‡
1/600	600 to 1300	60%	4	60°	650	60%
1/300	300 to 600	70	2	60°	325	72
1/150	160	incomplete	1	60°	160	85
1/30	30	85*	1	17° 20′	30	88**

Ang. disp. = radians per 10^7A. I = percent of monchromatic incident green light in emergent beam. ‡ Data from Baly. Absorption disregarded. * Transmission replica. ** Estimate.

To make these figures more useful they are given in Table I with data on the associated angular dispersions and, for comparison, values of I and of angular dispersion for certain prisms. Recalling that the angular dispersion of a grating is $d\beta/d\lambda = m/a \cos \beta$, we note that, even though the grating space and the order of spectrum are given, the dispersion may vary over a range of at least 4 to 1 with useful values of β. For this reason approximate limiting values are given, within which the gratings which were measured showed the stated intrinsic brightness.

For prisms the intrinsic brightness has been taken from Baly's *Spectroscopy*, where the values given are derived by computation from a consideration of surface losses alone. Although this served his purpose, it is not adequate when prisms are to be compared with gratings, and this is particularly true when large prisms of dense glass are to be used, since much additional light is then lost by absorption. If corrected for absorption, Baly's values of I would be appreciably reduced.

In contrast to the bright gratings mentioned by Rowland, we now find rulings made bright by definite means of control. Although in a given instance repeated attempts are usually required in order to rule a grating with maximum brightness, it is fair to say that the product is no longer fortuitous.

The Application of Multiplier Photo-Tubes to Quantitative Spectrochemical Analysis*

E. A. BOETTNER, *Wyandotte Chemicals Corporation, Wyandotte, Michigan*

AND

G. P. BREWINGTON, *Lawrence Institute of Technology, Detroit, Michigan*

INTRODUCTION

ONE of the principle advantages of spectrochemical analysis is the factor of speed. This is true especially in metallurgical analysis, where the analysis of a large number of samples in the shortest time is essential. At present the factor limiting the speed of analysis is the time required to process and photometer the film, and reduce the readings to results useful to the industry.

Several have already worked on the problem of eliminating the photographic plate. In 1940, Harrison discussed[1] the possibility of using photoelectric methods of line recording in place of the sensitized plate. Duffendack and Morris, in 1941,[2] described the investigation on the use of Geiger-Müller counters for a direct measurement on lines emitted from the spectrograph, while Rank, Pfister, and Coleman[3] reported on the use of a single multiplier photo-tube.

It is the purpose of this paper to describe the results of an investigation using two electron multiplier photo-tubes (RCA 931) for quantitative spectrochemical analysis when attached to a spectrograph.[4]

CIRCUIT

The RCA 931 tube is a high vacuum photo-tube in which the photo-current produced at the light-sensitive cathode is multiplied by secondary emission occurring at the 9 successive dynodes within the tube. The spectral sensitivity of the tube is shown in Fig. 1. A developmental multiplier photo-tube (C-7045) having an ultraviolet transparent envelope, is also used. No exact data on the spectral sensitivity of this tube are available, but approximate data, as supplied by the manufacturer, are shown in Fig. 1.

Any electrical circuit useful in spectroscopy should give an electrical current which is a linear function of the light intensity (photons per sec.) and the ratio of two such currents from separate photo-tubes should give the ratio of the intensities of the spectral lines exciting the two tubes. The familiar bridge suggests itself as the electrical circuit most adapted to make these measurements and is used in this work. The circuit used is shown in Fig. 2. It will be noted that the photo-tubes are connected in the arms of the bridge so that only the last stage forms a part of the bridge circuit. The two resistances forming the other arms of the bridge are variable wire wound resistances, but once proper values are chosen for these resistances they need not be changed unless the photo-tubes themselves are changed. The voltage supply system and voltage divider circuit are conventional. The voltage applied to either photo-tube is controlled by adjusting a variable resistance in series with the voltage divider resistance. A further advantage of the bridge circuit is the automatic cancelling out of small voltage supply irregularities. If a balance

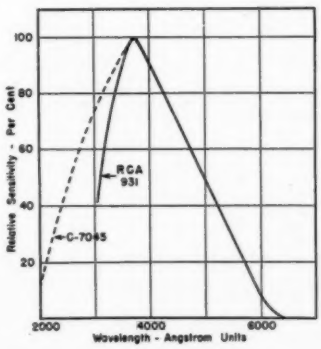

FIG. 1. Spectral sensitivity of the RCA 931 and the C-7045 electron multiplier photo-tubes.

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] G. R. Harrison, "Some future possibilities of spectrographic analysis," Conference on Spectroscopy and Its Applications, Cambridge, Massachusetts (1940).

[2] O. S. Duffendack and W. E. Morris, J. Opt. Soc. Am. **32**, 8–24 (1942).

[3] D. H. Rank, R. J. Pfister, and P. D. Coleman, J. Opt. Soc. Am. **32**, 390–396 (1942).

[4] E. A. Boettner and G. P. Brewington, Phys. Rev. **64**, 45 (1943).

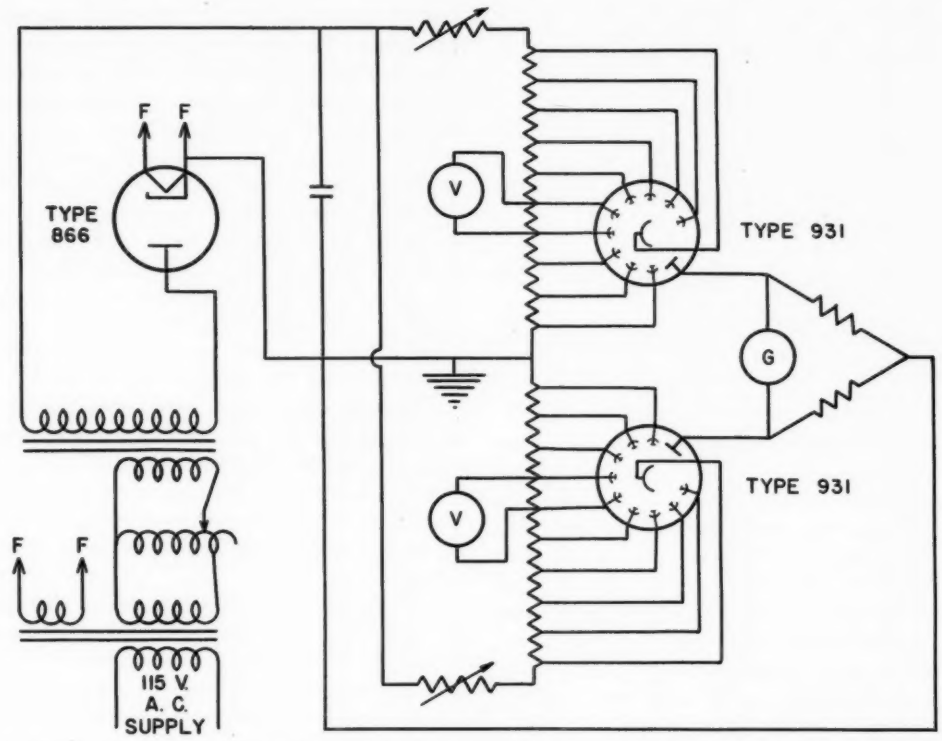

FIG. 2. Complete circuit using two electron multiplier photo-tubes connected in parallel with the rectifier tube and connected into a bridge to measure the ratio of output.

is established, the primary input voltage may vary several volts without the balance being seriously changed.

The galvanometer available had a short period and was much too sensitive. Small variations in the ratio of two lines, caused by conditions in the arc source, made the galvanometer very unsteady. An Ayrton shunt having the usual ratio taps but about half the critical external damping resistance of the galvanometer was constructed and proved quite satisfactory in reducing the galvanometer deflection and irregularities. The galvanometer, so shunted, serves to give the circuit the property of averaging the line intensities over several seconds of time, but still will indicate large fluctuations of line ratios originating from the source, so that they may be neglected in making the quantitative measurements.

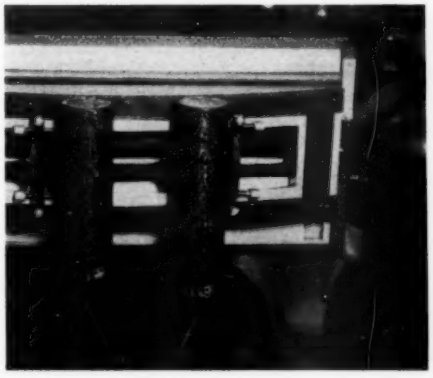

FIG. 3. Photo-tube housings.

EQUIPMENT

The spectrograph used is a concave replica grating spectrograph, having a focal length of 106 cm. The two tubes are placed in separate light-tight housings, each provided with a slow-motion screw, and made to travel on the camera track of the spectrograph. The light from the

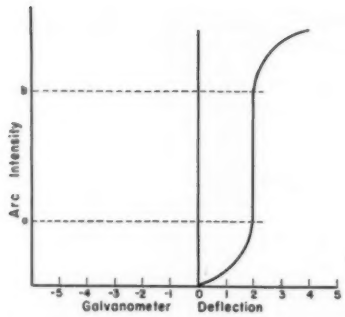

FIG. 4. Variation of output ratio (galvanometer deflection) of tubes with arc intensity, when located on 3968A Ca and 5390A Na lines of 25 percent sodium hydroxide burned in high voltage a.c. arc.

grating enters each housing through a slit 3 cm long and 0.6 mm wide. The mounts are placed approximately on the line to be measured by observing the lines visually and marking their position on the camera track. The exact location is found by turning on the circuit and arc, and moving the tube mounting slowly in the vicinity of the line by turning the adjusting screws at the side of the tube housing until a maximum deflection is obtained. The tube housings and the adjusting screws are shown in Fig. 3.

To connect the photo-tubes with the rectifying unit and galvanometer, two eleven-conduit cables five feet in length are used. They consist of eleven strands of silk-covered enameled Litz wire run through clear Transflex plastic tubing. The Litz wire was painted with a non-conducting paint for further insulation before the various strands were joined.

The spectrograph is set so as to utilize the same high voltage arc or spark as is routinely used in this laboratory.

CALIBRATION AND RESULTS

It was first planned to calibrate the galvanometer deflection, representing bridge unbalance, to give quantitative determinations directly. Such a method would be desirable to obtain extreme speed of analysis. However, due to fluctuations in the quality of light given off by the arc, this appeared impossible at the time.

Figure 4 illustrates qualitatively what happens in the high voltage a.c. arc for a material normally producing a galvanometer deflection of 2 cm. This is an example using carbon electrodes coated with sodium hydroxide with one phototube set at the 5890A sodium line and the other at the 3968A calcium line. The galvanometer scale is adjusted to read zero when no light enters the spectrograph. While the intensity of the arc remains between *a* and *b*, the galvanometer deflection is constant at 2 cm. However, the deflection occasionally drops to zero, in accordance with the portion of the curve below *a*. This is caused either by the arc stopping momentarily, or, more likely, the arc striking on a portion of bare carbon. When the latter occurs, the two lines being measured are partially or wholly eliminated and the galvanometer drifts to zero.

The deflections in the other direction, shown by the portion of the curve above *b*, occur when there is a large burst of light given off by the arc. When this occurs, light of the matrix material (Na in this case) appears to be given off in increased proportions compared with the impurities.

Neither of these difficulties appears, when using self-electrodes and the high voltage spark, but other interferences are present so that the direct calibration of the galvanometer does not give results as accurate as the method of calibration to be described herein. A comparison of the results of both methods is shown later. It can be seen that this device shows instantaneous changes of the ratio of two spectral lines (galvanometer deflection in Fig. 4), and is therefore a valuable tool for studying the characteristics of spectrographic light sources.

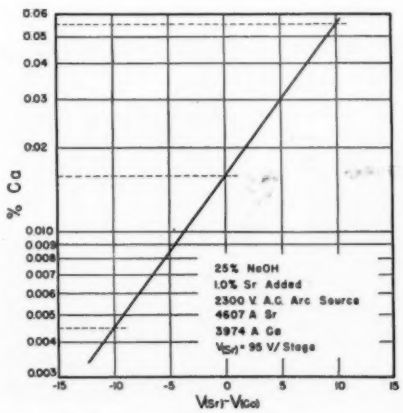

FIG. 5. A typical calibration curve.

The arc interferences described are partially eliminated by adding an internal standard to materials to be analyzed on carbon electrodes, and using a line from this source for one of the photo-tubes. This eliminates the effect resulting in the portion of the curve above *b*, caused by the matrix element. When self-electrodes are used, it is possible to use a line of the matrix material for calibration. To overcome the other difficulty, (the portion of Fig. 4 below *a*), the current output of the two tubes is held equal. This moves the entire curve to correspond with a vertical line passing through zero deflection. To do this, it is necessary to vary the sensitivity of the tubes as the ratio of intensity of the lines striking them varies. This is accomplished by varying the input voltage to the tube receiving the impurity line, while holding the voltage of the internal standard tube fairly constant (±1 volt per stage). If the tubes are so balanced, and the ratio of intensity of the two lines remains constant, the output of each tube varies with the intensity of the arc, but the ratio of output of the two tubes remains zero.

In the present circuit the difference in the voltage per stage of the two tubes, when the bridge is balanced at zero, is used as an indication of the ratio of light radiation striking the two tubes. If the potential applied to the internal standard tube can be held constant, the voltage per stage of the impurity tube can be plotted directly as a function of concentration. However, no effort was made to do this in this project. In the work described here, the potential applied to the internal standard tube is permitted to vary as much as two volts per stage.

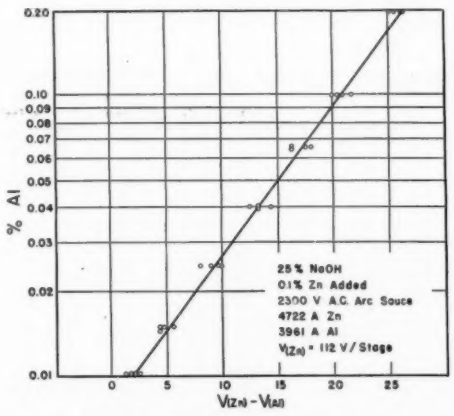

FIG. 6. The calibration curve of aluminum in 25 percent sodium hydroxide.

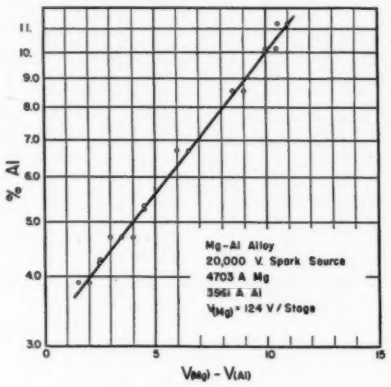

FIG. 7. The calibration of aluminum in Dowmetal.

TABLE I.

Sample No.	% Al added	*V*(Zn)	*V*(Al)	*V*(Zn) − *V*(Al)	% Al found	% deviation
01	0.11	115	93	22	0.12	8
		113	93	20	0.093	16
03	0.009	113	113	0	0.008	11
		112	110	2	0.010	11
05	0.017	115	108	7	0.018	6
		114.5	108	6.5	0.017	0
		115	107.5	7.5	0.019	12
		115	109	6	0.017	0
06	0.18	113	87	26	0.16	11
		114	87	27	0.18	0
07	0.038	103.5	96.5	+7	0.036	5
		96	89	+7	0.036	5
08	0.012	100	99.5	+0.5	0.013	8
		100	100.5	−0.5	0.0115	4
09	0.081	100.5	87	13.5	0.085	5
		100	87.5	12.5	0.075	7
10	0.135	100	82	18	0.155	15
		100	83	17	0.14	4
					Average deviation	7.2%

The calibration curve for an element is obtained by burning a series of known samples in the arc and obtaining the potential which must be applied to the impurity photo-tube for bridge balance while a nearly constant potential (±1 volt) is applied to the internal standard tube. A typical calibration curve is illustrated in Fig. 5. This is a calibration for the determination of Ca

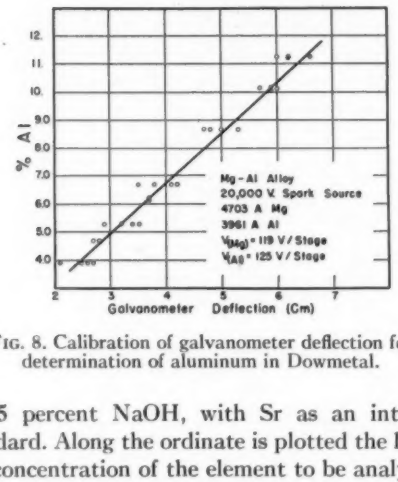

FIG. 8. Calibration of galvanometer deflection for determination of aluminum in Dowmetal.

in 25 percent NaOH, with Sr as an internal standard. Along the ordinate is plotted the log of the concentration of the element to be analyzed, and along the abscissa is plotted the voltage difference per stage of the two tubes, i.e., the voltage per stage of the internal standard tube minus the voltage per stage of the tube receiving the impurity lines. It will be noted that at 0.016 percent Ca, the current output of the two tubes is equal when equal potential is applied to each tube. At 0.055 percent Ca, the output is equal when 10 volts per stage less is applied to the impurity tube, while at 0.0046 percent Ca, the output of the two tubes is equal when 10 volts per stage more is applied to the impurity tube.

To obtain a homogeneous mixture, sodium hydroxide solutions containing Al as the impurity and Zn as the internal standard were prepared. The resulting calibration is shown in Fig. 6. The average deviation of the points from this curve is 7 percent. A number of samples were then analyzed from this curve. The results are shown in Table I.

Because of the interest of metallurgical industries in rapid analyses, it was decided to try this device for the analysis of metals. The low dispersion spectrograph limited the metal to the non-ferrous types, so magnesium alloys were chosen. A group of carefully analyzed Dowmetal samples was obtained from The Dow Chemical Company for this purpose. A 1-kw uncontrolled spark source having a 0.0025-μf capacitance in parallel with the spark was used. The photo-tube circuit was balanced after sparking the samples for 45 seconds and the voltage readings recorded for each tube. The calibration curve for aluminum in Dowmetal is shown in Fig. 7. The maximum variation of the points from the curve is 6 percent, with an average variation of 3 percent. A group of three samples was then run, using this calibration curve, to test for reproduceability. To do this, the same electrodes of each sample were used, filing down the surface after each exposure. The photo-tube circuit was thrown out of balance after each set of readings. The results of this run are shown in Table II.

The direct calibration of galvanometer deflections in terms of percent composition was tried on the same samples. To do this, the voltage applied to each tube was held constant, and the galvanometer deflection recorded for the various concentrations of one element in a number of samples at the end of a short period of sparking. The same aluminum and magnesium lines were used as in Fig. 7. The data are shown in Fig. 8. Here the maximum variations of the points from the curve are 12 percent. The precision in this case is only about half as good as in the balanced-bridge method. While this method shows some promise with the proper spark source, the balanced bridge appears to offer somewhat better accuracy.

The C-7045 tube was used for the determination of zinc in Dowmetal, using the 3302A Zn line. The standard 931 tube was not sensitive to this line in a sample containing 3 percent zinc, indicating that the lime-glass bulb is absorbing much of the radiation at this wave-length. The C-7045 tube was placed to receive the radiation of the 3302A Zn line, while a standard 931 tube was used for the internal standard line, in this

TABLE II.

Sample No.	% Al present	$V(Mg)-V(Al)$	% Al found	% deviation
47	5.6	5.5	6.0	7.1
		5	5.7	1.8
		4.5	5.3	5.4
		4.5	5.3	5.4
89	6.35	5.5	6.0	5.5
		5.5	6.0	5.5
		6.0	6.3	0.8
		6.5	6.6	8.9
34	10.2	9.5	9.6	5.9
		10.5	10.6	4.0
		10.5	10.6	4.0
		10.0	10.0	2.0
			Average deviation	4.7%

case the 4703A magnesium line. The resulting calibration curve is shown in Fig. 9. The bending-off of this curve is caused by the continuous background radiation, which is considerable because of the wide entrance slit used. The current output of the tube at 0.1 percent Zn is due entirely to the continuous background from the arc, while in the sample containing 0.8 percent Zn, the Zn line represents approximately 50 percent of the radiation striking the tube. The accuracy at the top of the curve is comparable with that obtained on the Al calibration, but falls off going down the curve as the background presents greater interference. This background effect is present when using the photographic plate for recording the lines, but is not as predominate because of the lesser slit widths used.

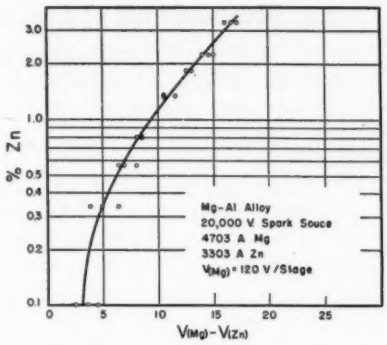

FIG. 9. Calibration of zinc in Dowmetal.

SENSITIVITY

The primary purpose of this investigation was to develop a circuit and method whereby the electron multiplier tubes could be used for quantitative analysis. However, some information was collected as to the sensitivity of the method to give an indication of what might be expected. These data are summarized in Table III. As the circuit and equipment used can make accurate measurements down to a three-microampere output from the photo-tubes, the limiting factor governing the sensitivity is usually the continuous background radiation of the source. If the circuit should become a limiting factor, there remains the possibility of amplifying the output of the tubes to keep them in a measurable range.

TABLE III.

Tube	Element	Matrix	Source	Line used	% detected	μ amp.
931	Ca	25% NaOH	a.c. arc	3968A	0.001	
931	Al	25% NaOH	a.c. arc	3961A	0.004 0.01	5
931	Al	Al-Mg alloy	Spark	3961A	4.0	35
C-7045	Si	25% NaOH	a.c. arc	2881A	0.1	

CONCLUSION

In conclusion, it can be stated that in every case illustrated, the governing factor of the sensitivity and accuracy has not been the tubes, but the supplementary equipment, principally the spectrograph and source.

The authors suggest that anyone caring to develop this method farther first build a spectrograph for this purpose. This would require a spectrograph of medium dispersion, of low resolution, and of as large an aperture as possible. By doing this, a greater amount of light through smaller slit widths would be striking the photo-tubes. This would improve both the sensitivity and the accuracy of the method. An extension of the circuit to measure several elements in a sample simultaneously would be desirable. Other improvements are obvious, especially in the photo-tube circuit, but they are of secondary nature.

The Measurement of Spectral Intensities in the Direct Current Arc*

ROBERT R. HAMPTON AND H. N. CAMPBELL
General Laboratories, United States Rubber Company, Passaic, New Jersey

IN quantitative spectrographic analysis of nonmetallic samples, the low voltage direct current arc between graphite electrodes has certain advantages in sensitivity and convenience. However, many workers have preferred other sources for which better reproducibility is claimed, such as the condensed spark, and the so-called a.c. arc. It seemed probable that the greater precision of these sources might be due largely to the carefully controlled conditions under which they are usually operated, and that conditions might be found under which the d.c. arc would be equally reliable. A study has accordingly been made of the effects of certain arc variables on the reproducibility of spectral intensity measurements. In this paper the factor of sample composition (effect of "extraneous elements") is not considered; we are here concerned only with the ability to get reproducible measurements on a given sample.

By spectral intensity is meant the integrated total energy emitted as a single spectral line, rather than the ratio between selected line pairs. Of course, if two line intensities are constant, their ratio will be constant, but the reverse is not necessarily true.

APPARATUS

Intensities were measured photographically, with a Baird[1] 3-meter grating spectrograph, using the first-order range 2250–3650A, where the dispersion is 5.6A per mm, and an 0.050-mm slit width. A quartz lens, of 65-cm focal length, mounted about 15 cm from the slit, forms a 5× enlarged image of the arc at the grating. By diaphragming the grating and moving the arc stand up and down, it is possible to select the portion of the arc image to be used. An auxiliary glass lens images the arc on a calibrated screen, so it is possible to maintain the desired arc gap and position throughout each exposure.

The sector used in obtaining the plate calibration spectra has six steps differing by a factor of two, thus giving a seven-stepped spectrum including the open step above the edge of the sector. The sector is driven by an induction motor at a speed slightly less than the synchronous speed of 3600 r.p.m., and is mounted 14 cm from the slit, which is about as close as practicable, because of the recessed slit housing. Since the astigmatic focal point for this range is only about 6 cm from the slit, some astigmatism is thus introduced. However, even with the full grating height of 4 cm, this astigmatism is less than 1 mm, and causes no error when measurements are made in the center of the 3-mm spectrum steps, since the microphotometer used, a standard ARL model,[2] has a slit 1.1 mm by 0.012 mm. The grating is ordinarily diaphragmed to a height of 1 cm, which practically eliminates the astigmatism.

PHOTOMETRY

The essentials of photographic photometry have been thoroughly covered by Harrison,[3,4] who points out the desirability of a gamma of about 1.0. Since most microphotometers are not accurate at photographic densities higher than about 1.5, the use of high contrasts unnecessarily restricts the range of intensities which may be measured. At a gamma of 1.0 the microphotometer error is small in relation to the other errors, and higher contrast serves only to get an "empty magnification" of these errors without increasing the real accuracy, unless the microphotometer error is unusually high. With a good microphotometer it might be possible to increase the range of measurable intensities by using a gamma lower than 1.0. However, in experiments with some special plates having a gamma of 0.5, we found that the rather extensive toe and shoulder regions of the characteristic curves had such low contrast as to lower appreciably the precision of measurements.

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] W. S. Baird, *Proceedings of the Sixth Summer Conference on Spectroscopy and Its Application* (John Wiley & Sons, Inc., New York, 1939), p. 80.

[2] H. W. Dietert and J. Schuch, J. Opt. Soc. Am. **31**, 54 (1941).

[3] G. R. Harrison, J. Opt. Soc. Am. **19**, 267 (1929).

[4] G. R. Harrison, J. Opt. Soc. Am. **24**, 59 (1934).

It appears to be fairly common practice among spectroscopists to use a high contrast plate, such as Eastman Spectrum Analysis No. 1, and underdevelop, in order to secure a reasonably low contrast. This procedure has distinct disadvantages. The errors due to uneven development and Eberhard effect are increased, and careful control of development time, temperature, and agitation are necessary. Development is stopped on the very steep portion of the curve of time *versus* degree of development, so that slight changes in conditions have a very marked effect. These difficulties are avoided by using relatively low contrast plates and developing fully.

At present we use Eastman Spectrum Analysis No. 2 plates, although they have a somewhat higher gamma than desirable (about 1.3 with normal development—3½ minutes in D-19). Processing conditions are not critical; time and temperature of development may vary considerably without serious effects. The intermittency effect is very slight with these plates; lines differing in intensity by a factor of ten give parallel step-sector calibration curves. At the time this study was made Spectrum Analysis No. 2 plates were not available. We used special experimental Eastman plates, with a similar emulsion, but a contrast of about 1.0 and hence about twice the effective intensity range.

In order to measure intensities photographically, it is, of course, necessary to calibrate each plate. Where measurements are made relative to another intensity recorded on the same plate, as in the "internal standard" method of spectrographic analysis, it is only necessary to obtain a relative plate calibration. However, when it is desired to compare intensities recorded on different plates, it is necessary to use an "external standard," making the measurements in terms of some reproducible unit of intensity (whose absolute value need not be known.) Slavin[5] has described a constant intensity iron arc for this purpose, with which he gave timed exposures. We have found it more convenient to arc a weighed portion (10.0 mg) of cobalt oxide (Co_2O_3), in the same manner as a sample is arced for analysis, except that the rotating step sector is placed in front of the slit. The exposure is continued until the cobalt oxide is completely vaporized. Microphotometer readings for successive steps of the cobalt line at 3042.481A are plotted with log−log coordinates against equivalent mg Co_2O_3 (10.0×the corresponding sector aperture). A second similar curve is drawn for a weaker cobalt line at 3147.060A. Intensities for this line are converted to the Co 3042.481 basis by multiplying the actual "equivalent mg of Co_2O_3" by the ratio of the intensities corresponding to the straight line portions of the two curves at a microphotometer reading of 20 percent transmission. These converted intensities are then plotted against the corresponding microphotometer readings, as part of the same curve as the readings from Co 3042.481. With this graph microphotometer readings for test lines are converted to "equivalent mg Co_2O_3" as intensity units. In plotting these characteristic curves, background in the cobalt spectrum is ignored, since it is low, approximately constant, and may be considered as part of the total cobalt intensity.

Since all work reported here was with the same batch of plates, which had virtually constant contrast throughout the wave-length region investigated, it was considered permissible to make all measurements in terms of Co 3042.481.

The cobalt arc conditions had not been standardized at the beginning of this work. Each experiment was therefore made complete on a single plate so the results would be independent of changes in the cobalt arc. After optimum conditions had been established, the cobalt arc was found to be highly reproducible, as is discussed later.

ARC VARIABLES

Exclusive of sample composition, the arc variables which may be independently controlled are: electrode size and shape, region of the arc from which light is taken, arc gap length, and arc current. (Conceivably arc voltage might have been chosen rather than arc current, but the voltage is much less convenient to control.)

The electrode size and shape may readily be standardized. In order to investigate the other variables, a number of identical anodes, each containing known amounts of copper and manganese, were prepared as follows: A hole 0.200″ in diameter and 0.125″ deep was drilled in the

[5] M. Slavin, Ind. Eng. Chem. Anal. Ed. **12**, 131 (1940).

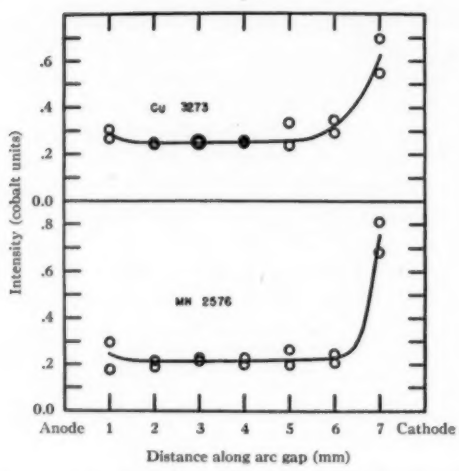

FIG. 1. Intensity variation along the arc keeping the total length constant. Intensity of light from 1-mm sections is plotted against distance from the anode.

end of a cylindrical graphite rod 0.25″ in diameter and about 1″ long. This hole was coated with an acryloid lacquer and 0.05 ml of a standard solution containing copper and manganese was added with a small all-glass hypodermic syringe. (The average error in measuring this solution is believed to be less than five percent.)

After the solution was added, the electrodes were dried in an oven at 70°C, heated red hot in a muffle furnace, and then allowed to cool. A graphite rod, given a blunt point with a pencil sharpener, was used as top electrode (cathode).

For each variable to be studied several of the prepared anodes were arced, systematically changing the variable being studied, while holding all other conditions constant, and measuring the resulting variations in line intensity. Arc current was maintained at 15.0 amperes except for the plate where the effects of arc current variation were being studied. In all cases, the electrodes were arced long enough to vaporize the sample completely.

It was considered probable that the intensities of arc and spark lines would not be identically affected by arc variations. This study has included the copper arc line at 3273.962A and the manganese spark line at 2576.104A. (In some cases Mn 2605.688 or Mn 2593.729 was used. These lines belong to the same triplet as Mn 2576.104 and would be expected to vary in the same way.)

Background measurements were made adjacent to each test line and the equivalent intensity (as read from the plate characteristic curve) subtracted from the corresponding line intensity, as described by Pierce and Nachtrieb.[6] The validity of this procedure has not been investigated, since the corrections were rather small and reasonably constant.

Intensity Variation Along the Arc Gap (Fig. 1)

Light was taken from a 1-mm high section of an 8-mm arc at varying distances from the anode. It was found that the intensity of light emitted is approximately constant throughout the length of the arc, except near the electrodes. There is a slight increase in intensity near the anode, and a large increase near the cathode.

Arc Gap Length

The effect of variation in the total length of the arc gap was studied for two cases: (1) the entire arc was imaged on the grating, and (2) a portion of the positive column was imaged on the grating.

When light from the whole arc was taken for

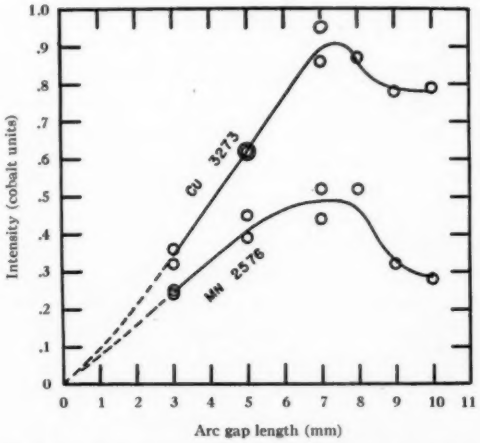

FIG. 2. Effect of arc gap length on intensity light taken from the whole arc. Note the drop in intensity when the arc becomes so long that the images of the ends of the arc no longer fall within the grating aperture.

[6] W. C. Pierce and N. H. Nachtrieb, Ind. Eng. Chem. Anal. Ed. **13**, 774 (1941).

analysis (Fig. 2), the intensity was approximately proportional to the arc length, for arc gaps less than about 7.5 mm. For arc gaps greater than 7.5 mm there was a sharp drop in intensity because of the fact that the whole arc was, in fact, no longer being used. With the lens used, the image of a 7.5-mm arc was magnified, so that the electrodes were imaged at the top and bottom of the grating, respectively. When the arc length was increased beyond 7.5 mm, the electrode images no longer fell on the grating and the intense light from near the electrodes was lost.

In studying the effect of arc length, using only the light from the positive column, a 2-mm portion of the arc was imaged on the grating. The arc length was varied in three ways: (*a*) symmetrically, keeping the distance of the cathode from the portion of the arc imaged on the grating twice as great as the distance of the anode (Fig. 3); (*b*) keeping the cathode 4 mm above the top of the 2-mm sampled portion of the arc and varying the anode position (Fig. 4); (*c*) keeping the anode 2 mm below the bottom of the sampled portion of the arc and varying the cathode position (Fig. 5).

The data show that, using only light from the positive column, the intensity is nearly independent of arc length variations, although, as might be expected, there is some indication of a slight decrease in intensity for longer arc gaps. It is, of course, important that the cathode distance be kept great enough (at least 2 mm) to avoid getting any of the intense cathode layer light.

As can be seen from Fig. 2, use of the whole arc requires very exact maintenance of the electrode positions so they will be imaged just at the edge of the grating. If the electrode image misses the grating, the more intense regions of the arc near the electrodes (particularly the cathode) will be lost, with consequent large variation in effective total intensity. In addition, as the arc wanders about the end of the cathode, it would be very difficult to get a constant proportion of the cathode layer light on the grating. These considerations decided against the use of the whole arc, although there are some indications that the effect of extraneous elements (other than the one being determined) may be less serious when the whole arc is used.

The use of the positive column gives considerably less sensitivity, relative to background, par-

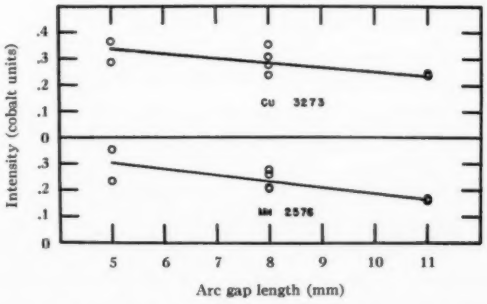

FIG. 3. Effect of arc gap length on intensity. Light taken from a portion of the positive column. Cathode distance kept equal to twice the anode distance and total length varied.

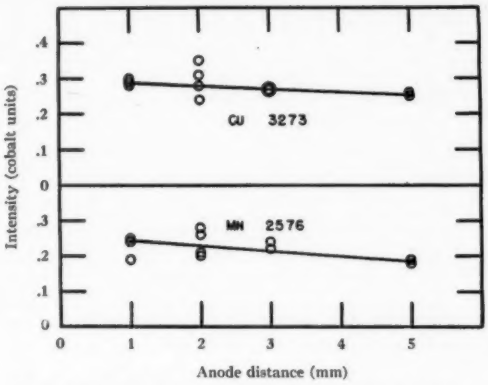

FIG. 4. Effect of arc gap length on intensity. Light taken from a portion of the positive column. The cathode distance was kept at 4 mm and the anode distance varied.

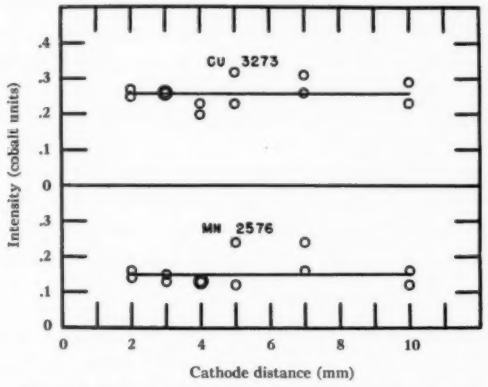

FIG. 5. Effect of arc gap length on intensity. Light was taken from a portion of the positive column. The anode distance was kept at 2 mm and the cathode distance varied.

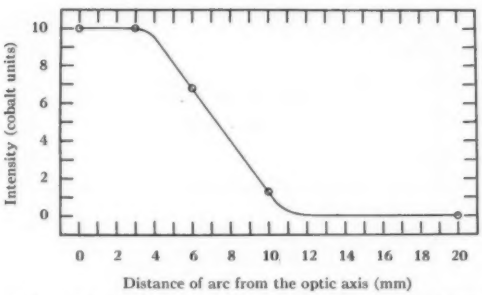

FIG. 6. Effect of arc wandering. Light intensity is plotted against the displacement of the arc from the optic axis. Slit width 50 microns.

ticularly for spark lines, than either the use of the whole arc, or of the cathode layer. Although we could easily increase the over-all intensity by using a wider diaphragm at the grating, faster plates, or moving the arc closer to the slit, none of these remedies would increase the ratio of line intensity to background intensity which is, of course, the limiting factor, given sufficient spectrographic speed, and large enough samples. However, the sensitivity of the positive column has been adequate for all our needs so far, including the routine determination of copper and manganese in concentrations as low as 0.5 p.p.m.

Arc Wandering (Fig. 6)

To evaluate the effect of lateral displacement of the arc from its normal position on the optic axis, a series of 10-mg samples of cobalt oxide was arced, with the arc about 1 meter from the slit, using a rotating pie sector, with a transmission of $\frac{1}{16}$, to reduce the intensity to a convenient value. The arc was moved farther from the optic axis for each successive shot. With a slit width of 0.050 mm, diffraction at the slit appears to have very little effect; the intensity drops rapidly when the arc is displaced far enough so that its geometrical image misses the grating. However, there appears to be sufficient leeway (± 4 mm) to provide a safe margin of error, in aligning the apparatus, and to take care of normal wandering of the arc. It is possible that with a very narrow slit, diffraction effects might increase the permissible margin of error in alignment.

Arc Current (Fig. 7)

In order to determine the effect of current fluctuations, a series of electrodes was arced, two at each of several different currents between 3 amperes and 24 amperes. The intensity of the manganese spark line at 2593.729A is approximately proportional to the arc amperage. The intensity of the copper arc line at 3273.962A is roughly proportional to the 0.7-power of the arc current.

It is evident that fairly careful current control is necessary. This is obtained by means of an automatic, solenoid operated, carbon pile rheostat[7] in series with the arc. An additional resistance, variable in steps between 7 and 11 ohms, is also in series with the arc. A manually operated carbon pile may be switched in to replace the automatic rheostat, when currents other than 15 amperes are desired.

The automatic rheostat holds current fluctuations to ± 2 percent, which represents a great improvement over fixed ballast resistors, and is much more convenient than careful manual control. Even closer regulation might be desirable and could probably be achieved by an a.c. network[8] in combination with a rectifier or by some type of electronic circuit. Either would be relatively expensive for the amount of power necessary.

It is probable that one of the principal advantages of the high voltage a.c. and d.c. arcs is that, because of the very large ballast resistance used, ordinary fluctuations in the voltage drop across the arc will have only a very slight effect on the arc current. This represents, however, an uneconomical and potentially dangerous method of obtaining constant current.

Optimum Arc Conditions

The actual value of the arc current is not critical, provided that it is held constant at the selected value. The use of fifteen amperes with an anode diameter of $\frac{3}{16}$ inch gives a convenient rate of sample volatilization and a smoothly burning arc.

The total length of the arc gap is also not critical, provided that it is long enough so light from the regions near the electrodes is not imaged on the grating. We have standardized on an

[7] Obtained from the Safety Car Heating and Lighting Company, Inc., New York.

[8] L. C. Green and J. B. H. Kuper, Rev. Sci. Inst. **11**, 250 (1940).

8-mm gap, using only the light from the portion of the positive column between 2 and 4 mm above the anode.

PRECISION

When conditions are standardized as described above, and the current held constant by the regulator, the precision of the cobalt arc external standard is excellent. We have not made any careful study to select the most reproducible lines. The two lines used were selected as being lines of Co I of about the desired intensity and wave-length, and showing no obvious broadening. Statistical analysis of the data from two test plates, each with sixteen cobalt shots, showed a probable error for a single shot of about ±2 percent. No study has been made of reproducibility over long periods of time, but any change in optical conditions should affect both standard and sample to the same extent.

In connection with some unpublished work on the action of spectrographic buffers, in one group of about 150 intensity measurements for small amounts of various elements, statistical analysis showed a probable error of about ±5 percent for a single measurement. This is of the same order of magnitude as the error to be expected in measuring out the 0.050 ml of solution in which the test element was added to the electrode. It seems reasonable to expect the same probable error (about ±2 percent) as for the cobalt arc, for replicate analyses of a single homogeneous sample, on one plate, and a slightly larger probable error (probably about ±3 percent) for replicate analyses on different plates. This precision compares favorably with the best results for the spark and a.c. arc, and might possibly be improved by still more precise current control.

Cobalt oxide was selected for an external standard because it is available, has lines of the right intensity in all wave-length regions used for analytical work, vaporizes smoothly in the arc (in contrast to iron oxide which tends to sputter badly), and is not an element that we often have occasion to determine. (It would be undesirable to arc frequently large samples of a metal, such as iron, for which we make routine determinations of traces, because of the possibility of contamination from the air and electrode clamps.) Presumably, other elements than cobalt would be equally satisfactory.

The mercury arc[9] and helium lamp[10] which have been used as external standards do not have spectra sufficiently rich in lines to be very satisfactory. A discharge lamp containing one of the other inert gases, with a richer ultraviolet spectrum, might make the best external standard, if sufficient constancy and intensity could be obtained. It would probably be desirable to use such a lamp as a secondary working standard, making occasional replicate comparisons with a primary standard, such as the cobalt arc, which is not subject to aging and deterioration.

ELECTRODES

Although for the experiments described above, electrodes $\frac{1}{4}$ inch in diameter were used, we have found that an anode with a diameter of $\frac{3}{16}$ inch gives a somewhat steadier and hotter arc, and is large enough to accommodate a suitable size sample. For all routine work, anodes are shaped as shown in Fig. 8.

An electrode cutter (Fig. 9) was constructed

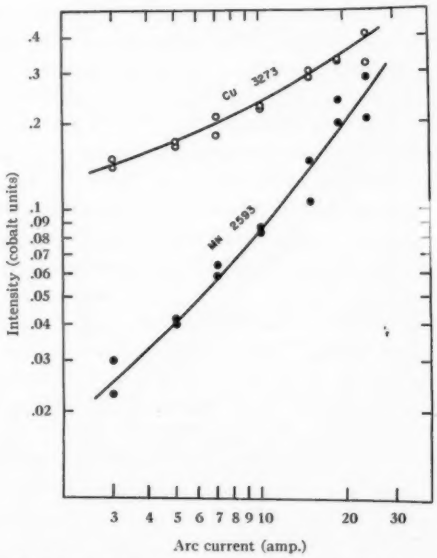

FIG. 7. Effect of arc current on line intensity using light from a portion of the positive column.

[9] M. Slavin, Ind. Eng. Chem. Anal. Ed. **10**, 407 (1938).
[10] O. S. Duffendack and R. A. Wolfe, *Proceedings of the Sixth Summer Conference on Spectroscopy and Its Application* (John Wiley & Sons, Inc., New York, 1939), p. 97.

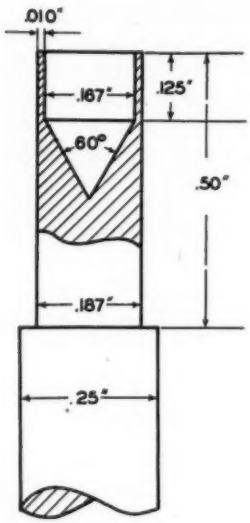

FIG. 8. Anode dimensions used for routine analyses.

according to a modification of the design recommended by Myers and Brunstetter.[11] The construction was made somewhat heavier, and the outer cutting edges were given a slight inward slant to overcome any tendency to throw the electrodes to the side. The facing cutter was made as a separable part, for ease in sharpening, and a slight reverse taper (about 1 : 100) was given to the central cylindrical portion of the outer cutter and to the inner drill, to lessen breakage of the electrode walls.

In order to cut walls as thin as 0.010" (which is desirable in order to minimize the continuous spectral background, as well as the effect of any impurities in the graphite), it is necessary that the cutter be accurately made, and rotated smoothly. Considerable difficulty was experienced, due to warping during heat treatment, when plain carbon steel was used in making a cutter. It was finally found that by using a nondeforming oil hardening tool steel (Carpenter Steel Company, *Hampden*) satisfactorily accurate cutters could be easily prepared. Owing to its hardness, this tool steel has the additional advantage of wearing at least five times as long as plain carbon steel, before resharpening is necessary. As many as 1000 electrodes may be cut before the cutter becomes dull. This steel is also mildly corrosion-resistant.

The cutter is mounted on the shaft of a $\frac{1}{4}$-horsepower motor, operating at 1800 r.p.m. The principal reason for using such a heavy motor, is to get a steady, vibration-free mounting, as any appreciable wobble of the cutter head is fatal to thin-walled electrodes. A transparent plastic guard (not shown in the photograph) covers the cutter head for safety. The graphite powder falls into a receptacle beneath the cutter. Cathodes are prepared with a point 1 or 2 mm in diameter, from $\frac{1}{4}$" graphite rods, by means of a pencil sharpener.

For use in the routine determination of copper, manganese, and iron, electrodes are shaped from the National Carbon Company's "Regular Spectroscopic" grade of graphite rods, and then purified in batches of about 300 by acid treatment in an extractor.[12] To prevent crushing, the electrodes are packed in 100-ml beakers, which are

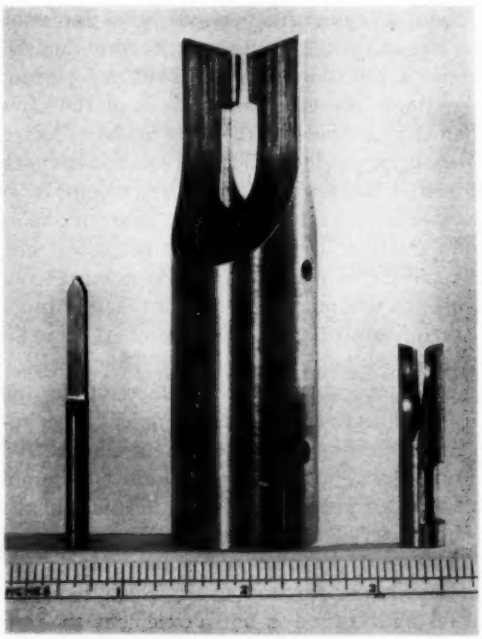

FIG. 9. Electrode cutter parts.

[11] A. T. Myers and B. C. Brunstetter, Ind. Eng. Chem. Anal. Ed. 11, 218 (1939).

[12] The design for this extractor was suggested by Dr. J. A. Baty of this laboratory, who has also participated in numerous helpful discussions on various phases of this work.

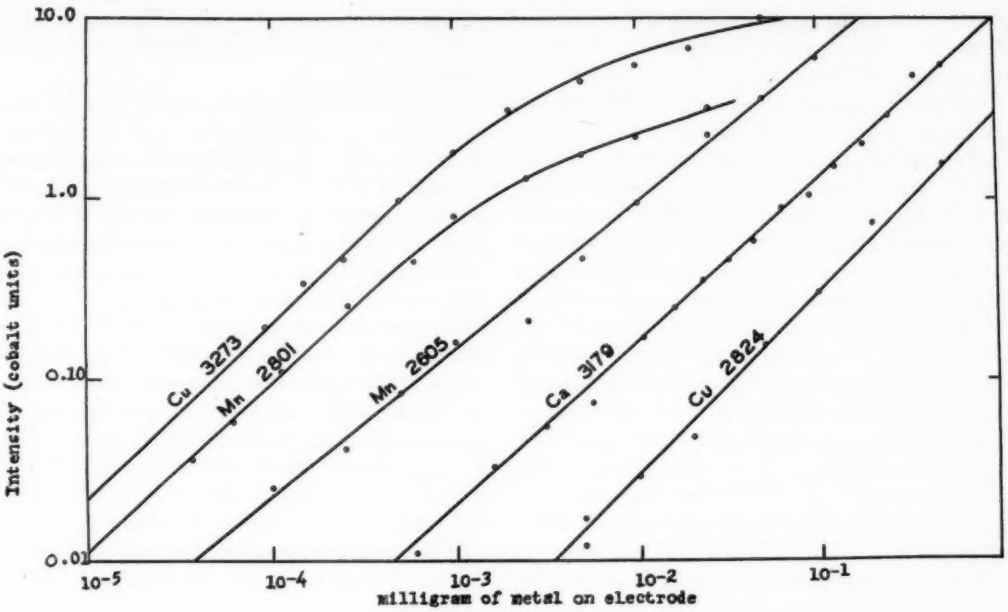

FIG. 10. Typical analytical working curves.

stacked in the extractor. The electrodes are continuously immersed in acid vapor and wet with a stream of hot acid condensate, which runs down through holes in the bottoms of the beakers. The electrodes are extracted for twenty-four hours with concentrated nitric acid, and then for six days with constant boiling (6 : 5) hydrochloric acid. They are then extracted for a few hours with water, and oven dried, before removal from the extraction beakers.

This extraction treatment satisfactorily removes Cu and Fe; most of the other elements which are of interest in our work are not found in the unpurified electrodes. Ca, Mg, and Ti are partially but not completely removed. B and Si are scarcely affected by the extraction.

APPLICATIONS

The general procedure for intensity measurement, developed as described above, has been applied to several specific analytical methods, typical of which is one for the determination of Cu, Mn, Fe, Zn, and Ca in organic materials. A weighed sample (pelleted, if solid) is ashed directly in an electrode containing 10.0 mg of buffer (a fifty-fifty mixture of lithium and strontium carbonates), and then arced. Analytical working curves are prepared by plotting, on log−log coordinates, intensity of the test line in cobalt units ("equivalent mg Co_2O_3") against weight of metal on the electrode. Data for these curves are obtained by adding known amounts of a series of standard metal solutions to lacquered electrodes containing buffer, drying, and arcing.

EXTERNAL STANDARD *VS* INTERNAL STANDARD

Some typical calibration curves are shown in Fig. 10. (These curves have been corrected by an assumed blank sufficient to make the lower part of the curve a straight line. The blank thus calculated checks the experimentally measured blank. With specially purified buffer chemicals the blank is extremely low, and frequently entirely negligible.) It will be noted that, with the exception of the curve for Cu 2824.369, none of the working curves has a 45° slope. This has been attributed by Pierce and Nachtrieb[6] to self-reversal. Probably the curvature at high intensities found for the Cu 3273.962 and Mn 2801.064 graphs is due to increased reversal. No two of the curves are

parallel, which presents a possible source of error in the internal standard method of analysis, if the sample weight varies greatly.

For two non-parallel curves, the ratio between the intensities of the corresponding two lines will vary with the total amount of sample, even though the actual ratio of the amounts of the two elements remains constant. In other words, in order to use the internal standard method, it is desirable either to keep the sample weight constant, or select an internal standard line which gives a curve parallel to the curve for the test line. In addition, for the internal standard method, it is necessary to measure separately the amount of sample and the amount of standard element, and to measure the intensity for standard and test element, for each analysis. Unless one is working with solutions, there is considerable difficulty in introducing the internal standard element.

With the external standard method, the standard intensity measurement is automatically included in the plate calibration. For each analysis only one weighing and one intensity measurement are necessary.

If the internal standard would actually compensate for variations in conditions, it might still be worth while, but it is, in fact, frequently impossible to find an element of the same volatility as the test element and with a test line of suitable intensity in the right wave-length region. Such an internal standard line, if found, would probably not be affected in the same way as the test line by extraneous elements, which are the most serious variables, with a carefully controlled arc.

For these reasons we consider the external standard method definitely superior in convenience and accuracy, except possibly where a suitable internal standard element is already present in the sample. Where metallic electrodes are being analyzed, it is, of course, necessary to use the internal standard method, because of the uncertainty regarding the quantity of sample vaporized.

International Commission on Illumination

AT the annual meeting of the United States National Committee of the International Commission on Illumination held November 10, 1943, the following officers were re-elected:

President, PRESTON S. MILLAR, *Electrical Testing Laboratories, Inc.*
Vice President, F. C. BRECKENRIDGE, *National Bureau of Standards*
Secretary-Treasurer, G. H. STICKNEY, *Consulting Engineer*
Executive Secretary, A. A. BRAINERD, *Philadelphia Electric Company.*

This United States Committee has published an all-English version of the proceedings of the international meeting held in Holland in 1939. Copies that have just become available may be obtained through the Executive Secretary. These record the latest stage of development of lighting throughout the world up to the beginning of the war and have reference value for people in the lighting industry.

The United States Committee is engaged in cultivating, in behalf of the international body, arrangements for technical interchange of lighting information with leading engineers in the other Americas.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 1 JANUARY, 1944

Spectrochemical Analysis of Metals with the Multisource Unit*

M. F. HASLER AND J. W. KEMP
Applied Research Laboratories, Glendale, California

IN any discussion of sources for spectrographic analysis, there are four features to be considered: precision, sensitivity, range, and the influence of one element on another. The phenomena taking place in a source can be divided into those taking place on the electrode, and those in the discharge proper. Sources can be divided into two broad classes, arc-like and spark-like. The relations of these factors to each other are shown in a general way in Table I.

In order to obtain one of the four desirable qualities, one or more of the others must be sacrificed. For instance, in an arc analysis, the influence of one element on another can be reduced by dilution with a spectroscopic buffer, but this also reduces the sensitivity. In a conventional spark source, sensitivity may be increased by the use of higher inductance, but this makes the discharge more arc-like, thereby possibly reducing precision and increasing the effect of one element on another. The conclusion to be drawn from these considerations is that there is no one best source.

This same conclusion can be drawn from another situation encountered in practice. It is well known that, if a source is varying in any manner, lines of very different excitation energies will vary in different ways. As shown in Fig. 1, the most sensitive arc lines of the elements lie in the range 600A to 8500A, and the most sensitive spark lines from 200A to 4500A.[1,2] If it were possible (in a practical manner) to obtain with one exposure this entire range, a source designed for the analysis of several elements would not have to be too accurately controlled. It would be possible to choose internal standard lines and working lines with about the same excitation potentials. In practice, however, in order to obtain sufficient dispersion and a convenient size of film or plate, only 1500 to 3000 angstroms can be photographed as a single exposure. In any case, the region below 2000A is available only to vacuum equipment, and lack of proper photographic emulsions limits the portion of the remaining 6000 angstroms that can be used with ease in a single exposure. Therefore, the analyst must use arc and spark lines in the same exposure in order to analyze successfully for more than a very few elements.

Because of these difficulties, the analyst has been forced to make a choice between two extremes, arc and spark sources, sacrificing sensitivity for precision, or vice versa, etc. The authors believe that, with the controlled multisource, it is possible to make a compromise between the two extremes, rather than a choice. It has been shown[3] that it is possible with this unit to obtain spectra representing an almost continuous gradation from arc-like to spark-like, and that high precision can be obtained with high sensitivity in the case of aluminum alloys. It should be made clear that the multisource is not a combination of standard source units, but a single unit based on a new principle. The present work is concerned with extending data on the use of the multisource for the analysis of a wide variety of materials. Although a compromise still has to be made in choosing a source for a particular analysis, the authors wish to show that the new source unit has the following advantages: (1) Since each analytical problem represents a compromise among the features shown in Table I, better results can be obtained with a unit that offers an almost continuous array of discharges from arc-like to spark-like. (2) When high sensitivity is required for a particular element, it is not necessary to sacrifice precision and range, and to tolerate interference phenomena to such an extent that the method is undesirable for close quantitative control. (3) One source unit may be used for a wide variety of analytical problems.

Another difficulty encountered but not often emphasized is in detecting, and correcting for,

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh Pennsylvania, October 7–9, 1943.

[1] W. F. Meggers, J. Opt. Soc. Am. **31**, 39–46 (1941).

[2] W. F. Meggers, J. Opt. Soc. Am. **31**, 605–11 (1941).

[3] M. F. Hasler and H. W. Dietert, J. Opt. Soc. Am. **33**, 218–28 (1943).

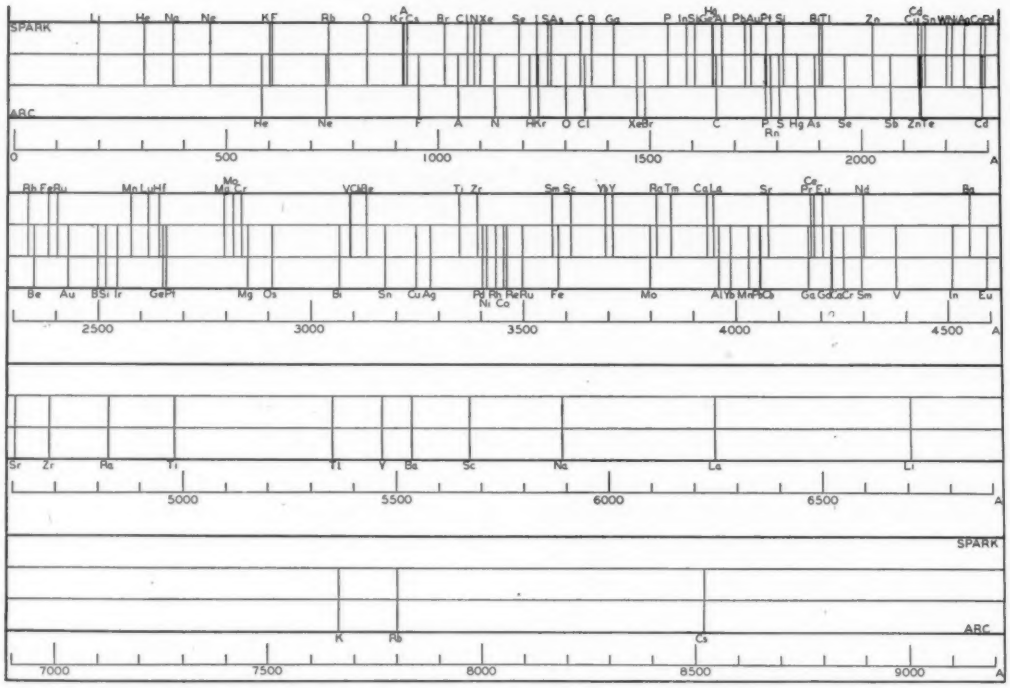

FIG. 1.

TABLE I. Correlation of source factors in quantitative spectrographic analysis.

		Precision	Sensitivity	Range	Influence of one element on another
Arc-like source	Electrode phenomena	Low because of erratic wandering of arc and erratic conduction of heat away from the tip	Large amount of material contributed to discharge		High because of effect of varying amounts of elements on fractional distillation process
Arc-like source	Discharge phenomena	Should be capable of high precision	High because of high concentration of material in discharge and high absolute sensitivity of arc lines	Limited by self-absorption	High because of high concentration of material compared to the amount of energy available for excitation
Spark-like source	Electrode phenomena	High because many hundred portions are sampled for each exposure	Small amount of material contributed to discharge		Little because fractional distillation as such has little to do with getting the sample into the discharge
Spark-like source	Discharge phenomena	High if each spark is controlled so that the total is a summation of identical discharges	Low because of low concentration of material in discharge and many sensitive spark lines are in the vacuum region	Limited by low sensitivity	Little because of low concentration of material and large amount of energy available

TABLE II. Standard and special conditions used in the analysis of metals with the controlled multisource.

Spectrograph: Applied Research Labs. —Dietert grating spectrograph, 2360–4580Å region.	Sample form:	disks	7/32" rods
Densitometer: Applied Research Labs. —Dietert projection-comparator densitometer.	Cooling:	none	cooled during exposure
Source: Applied Research Labs.— Dietert controlled multisource	Upper electrode:	sample	sample (150° truncated cone)
Peak voltage, secondary power circuit: 940 volts	Lower electrode:	National Carbon Co. Special graphite Spectroscopic electrodes ¼"	sample (150° truncated cone)
Slit: 60 microns	Analytical gap:	2 mm	3 mm
Lens: none	Apertures:	One at secondary focus and a second one-half inch in front of analytical gap (0.060")	One 0.060" at secondary focus
Film: Special Eastman Experimental Spectrum No. 2			
Developer: D19			
Development conditions: 3 minutes at 70°F			
Contrast: 1.2–1.3			
Calibration: calibrated iron spectrum given the same exposure time as samples			

Material	Capacitance (microfarads)	Inductance (microhenries)	Resistance (ohms)	Pre-exposure discharge time (sec.)	Exposure time (sec.)	Exposures per spectrum	Lower electrode	Circuit	Discharge type
Fe (rods)	2	50	0.4	10	30	1		oscillating	spark-like
Fe (disks)	4	180	10	10	30	1	120° cone	oscillating	spark-like
Cu, Fe, Mg Zn (disks)	5	100	10	10	30	1	120° cone	critically damped	spark-like
Al, Fe, Mg Zn (disks)	5	480	100	10	30	1	120° cone	overdamped	spark-like
Cu (disks)	5	480	100	30	30	1	120° cone	overdamped	spark-like
Fe (rods)*	40	480	50	3	10	1		overdamped	arc-like
Fe (disks)	40	480	50	3	5	2	120° cone	overdamped	arc-like
Al, Mg, Cu (disks)	60	480	50	3	5	2	20° cone	overdamped	arc-like
Zn (disks)**	60	480	50	0	5	1	20° cone	overdamped	arc-like

* Upper electrode negative, positive in all other cases.
** Sample in form of raised 60° cone on surface of sample.

differences in metallurgical history of samples of the same type of alloy.[4] One type of source may work very well for several types of alloys and different base metals, and yet fail to give sufficiently correct analyses on another type. Often poor working curves are obtained with a particular source, the difficulties being attributed to segregation, poor analysis of standards, effect of one element on another, etc., while the real difficulty is in the metallurgical form of the sample. In order to study this effect, it is advantageous to be able to eliminate it at least for certain phases of the work. The convenient way to do this is to have a source unit available that will give a large variety of sources to work with, some of which may minimize the effect mentioned above. This problem will be considered in greater detail under the analysis of aluminum bronze.

Turning to the experimental data, Table II gives the standard conditions used, optical, photographic; the types of alloys studied; and various special conditions employed. Certain of these conditions are significant. When the terms "arc-like" and "spark-like" are used in describing

[4] T. M. Hess and L. G. Reinhardt, "Spectrographic analysis of magnesium alloys." Paper presented at the 1943 meeting of the Optical Society of America, Pittsburgh, Pennsylvania.

TABLE III. Data for the analysis of steel rods.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
			a. c=2 μf, L=50 μh, R=0.4 ohm.				
Ni	3414.8	0.04%	3414.8/3009.6		0.1 –1.5%	1.38%	1.1%
Cr	4254.3	0.03	2822.4/3009.6	0.13 –2.8%		0.79	1.4
Mn	2576.1	0.01	2933.1/3009.6	0.2 –1.5		0.385	1.6
Mo	3684.1	0.02	2816.2/3009.6	0.14 –1.2		0.43	
	2816.2	0.04					
Si	2881.6	0.05	2881.6/3009.6	0.12 –0.43			1.7
V	4379.2	0.06	3102.3/3009.6	0.025 –0.30		0.175	1.4
	3093.1	0.004					
Cu	3274.0	0.004	3274.0/3009.6		0.015–0.22		1.4
			b. C=40 μf, L=480 μh, R=50 ohms.				
Ni	3414.8	0.002%	3414.8/3200.5	0.004 –0.2%	0.2 –3.0%	0.38%	2.6%
Cr	4254.3	0.0008	2677.2/2506.1	0.011 –0.15	0.15 –2.7	0.415	2.4
Mn	2576.1	0.004	4041.4/4216.2	0.25 –1.6		0.325	1.5
Mo	3684.1	0.002	2816.2/3200.5	0.02 –0.1	0.1 –1.0		
	2816.2	0.01					
Si	2881.6	0.003	2881.6/3200.5	0.013 –0.44		0.39	1.2
V	4379.2	0.003	4379.2/4375.9	0.0025–0.27		0.19	2.3
	3093.1	0.002					
Cu	3274.0	0.0002	3274.0/3200.5	0.018 –0.21		0.305	

* Percent at which the intensity ratio of the line pair given is equal to one.

a source, they refer only to the general appearance of the spectrum obtained with that source. The circuit conditions given here are not necessarily the best conditions available; however, they illustrate adequately the variety and excellence of results obtainable. It has been found in using a flat disk of metal and a graphite lower electrode in a Petrey stand,[5] that better reproducibility is obtained by using the purest grade of graphite available. This is related to the greater physical uniformity of the pure product in comparison to the ordinary grade of spectroscopic graphite. Two types of lowers were used, the first an approximately 150° cone, the second a 20° conical electrode with a hemispherical end. In the case of zinc, high sensitivity and high precision were obtained in the arc-like case by cutting a circular depression in the surface of the disk leaving a 60° cone projecting with its tip flush with the disk surface.

The first system to be discussed is the analysis of steel. The Bureau of Standards series of steel standards was used in most of this work. Table III gives sensitivity, precision, and range data for the analysis of $\frac{7}{32}''$ steel rods, using a spark-like and an arc-like source. We have found that a weak line can be conveniently used if the intensity of the line plus background is 1.3 times the intensity of the background measured next to the line. This corresponds to a line intensity, corrected for background, of 0.3-background intensity. The figure given, then, is the concentration in percent at which the above-defined intensity is obtained with a primary slit width of 60 microns on our spectrograph. It is possible in certain cases to obtain results at one-third of this value. In a survey of this sort, it is not convenient to determine precision by means of a laboriously large number of repeat runs. Therefore the figure given here represents the percent average deviation from the mean for eight repeat runs, rather than the standard deviation.

The working curves have been plotted on log-log paper, background correction being made in all cases. (See Fig. 2, etc.) Theoretically, the working curves should be straight lines at 45°, or, in case of self-absorption, should fit a curve of the form:

$$\text{Intensity ratio} = k_1(1-e^{ck_2}),$$

where c is the concentration, k_1 a proportionality constant, and k_2 a constant depending on the degree of self-absorption. Given in Table III and succeeding tables are the ranges in concentration over which the working curves are linear with the line pair noted, the range over which

[5] H. V. Churchill and J. R. Churchill, J. Opt. Soc. Am. **31**, 611–19 (1941).

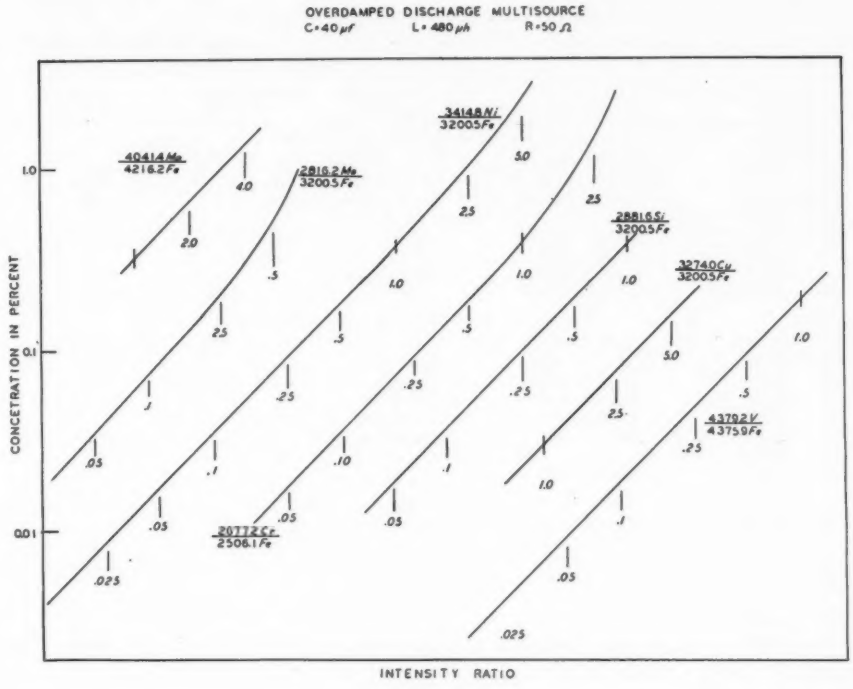

FIG. 2.

the curve showed self-absorption, and the index point. Referring again to Fig. 2, etc., the vertical scale, concentration in percent, is the same for all curves; the horizontal scale, intensity ratio, is of the same magnitude, but is adjusted horizontally for each curve, the values being represented by the small figures under each curve. It should be remembered that, although we are presenting some self-absorbed curves, a weaker line can usually be found, for higher concentrations of the element, which shows no self-absorption. The index point is given in the tables, and is represented on the curves by a short vertical line crossing the curve, this being the usual reference point at which the intensity ratio of the element line to the internal standard line is equal to one.

It might be well to mention at this point that many workers have had difficulty in analyzing for silicon in steel containing one percent or more chromium. In spark-like sources, the 2516.2A silicon line apparently has an iron line within 0.1A, making it unsuitable for analytical purposes. The 2881.9A chromium line usually interferes with the 2881.6A silicon line. The usual procedure is to reduce the primary slit width to eliminate the interference at the 2881.6A silicon line, but this increases densitometric errors. We believe the proper procedure is to choose a source that reduces the intensity of the interfering chromium line to the point where it no longer need be considered. In all of the spark-like cases studied here the 2516.2A silicon line had iron interference, but this is not so in the arc-like case. However, the case given in Table IIIa is the only one in which chromium interfered with the 2881.6A silicon line. In all other cases, including some quite spark-like ones, no interference was noted on this silicon line.

The arc-like case given in Table IIIb shows a degree of sensitivity approaching that of the d.c. arc. The precision, however, though not as good as the spark-like case considered, is considerably better than could be obtained with a d.c. arc between metal electrodes. This is an example of sacrificing precision for sensitivity,

TABLE IV. Data for the analysis of steel disks.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
			a. C=4 μf, L=480 μh, R=10 ohms.				
Ni	3414.8	0.01%	3493.0/3009.6		0.1 –1.3%		
Cr	4254.3	0.01	2822.4/2823/3	0.1 –1.0%	1.0 –2.8	1.2%	1.3%
Mn	4030.8	0.02	2933.1/3009.6	0.21 –0.6	0.6 –1.8	0.36	0.29
	2576.1	0.01					
Mo	2816.2	0.01	2816.2/3009.6		0.045–1.0		
Si	2881.6	0.02	2881.6/3009.6		0.011–0.5		1.5
V	3093.1	0.01	3093.1/3009.6	0.028–0.32		0.263	1.3
Cu	3274.0	0.002	3274.0/3009.6		0.013–0.26		2.0
			b. C=5 μf, L=480 μh, R=100 ohms.				
Ni	3414.8	0.06%	3414.8/3009.6		0.1 –3.6%	1.6%	1.3%
Cr	4254.3	0.02	2822.4/3009.6	0.16 –3.0%		1.15	0.99
Mn	4030.8	0.04	4034.5/3009.6		0.2 –1.7	0.98	1.0
Mo	2816.2	0.02	2816.2/3009.6	0.054–1.0		0.85	1.4
Si	2881.6	0.02	2881.6/3009.6	0.011–0.06	0.06 –0.4		1.7
V	4379.2	0.03	3093.1/3009.6	0.034–0.3		0.155	1.9
	3093.1	0.006					
Cu	3274.0	0.003	3274.0/3009.6		0.012–0.25	0.137	2.5
			c. C=40 μf, L=480 μh, R=50 ohms.				
Ni	3414.8	0.006%	3414.8/3009.6	0.053–0.5%	0.5 –4.2%	1.62%	1.7%
Cr	4254.3	0.002	2677.2/3009.6	0.014–0.3	0.3 –5.0	1.04	2.4
Mn			4034.5/3009.6		0.13 –2.0	0.58	2.9
Si	2881.6	0.003	2881.6/3009.6	0.012–0.2			3.6
V	4379.2	0.007	3093.1/3009.6	0.053–0.27			
	3093.1	0.004					
Cu	3274.0	0.006	3274.0/3009.6		0.015–0.3	0.415	
Mo			2816.2/3009.6	0.1 –1.1			

* Percent at which the intensity ratio of the line pair given is equal to one.

but it should be noted that the precision is still of the order of much good spark work and satisfactory for control analysis. Figure 2 gives the working curves for this case. They are very satisfactory, showing little self-absorption for a wide range of concentrations. The 3414.8A nickel line and the 4379.2A vanadium line, for instance, show none from 0.003 to 0.3 percent and nickel very little from 0.3 to 3 percent.

This is an excellent example of a set of conditions suitable for the thorough analysis of steel. With a single exposure good analyses can be obtained where formerly both the spark and either a.c. or d.c. arc would be required. This case amply demonstrates the extraordinary range of this source.

Table IV gives three cases investigated on steel disks using the Petrey stand method of handling samples. The first spark-like case (Table IVa) has a number of interesting possibilities. In the first place its sensitivity is sufficient so that it can be used for much routine steel analysis without resorting to second exposures under different discharge conditions. In the second place, the particular values of capacitance, inductance, and resistance used tend to cause the deposit of considerable amounts of carbon from the lower electrode on to the sample plate. Subsequent removal of sample is through this carbon layer. This phenomenon appears to eliminate certain changes of intensity ratio with changes of metallurgical history of the samples. This will be discussed in detail for the case of aluminum bronze. In any event, this property of the discharge should make it very suitable for fabricating stock analysis as well as for routine foundry analysis. No chromium interference on the 2881.6 silicon line was experienced. In the third place, this type of discharge gives very reproducible iron-to-iron line intensity ratios. Thus it makes an ideal source for film calibration and was used as such for all the work presented in this paper.

The second spark-like case given in Table IVb possesses about the same degree of precision in general as that given in IVa. However, many of

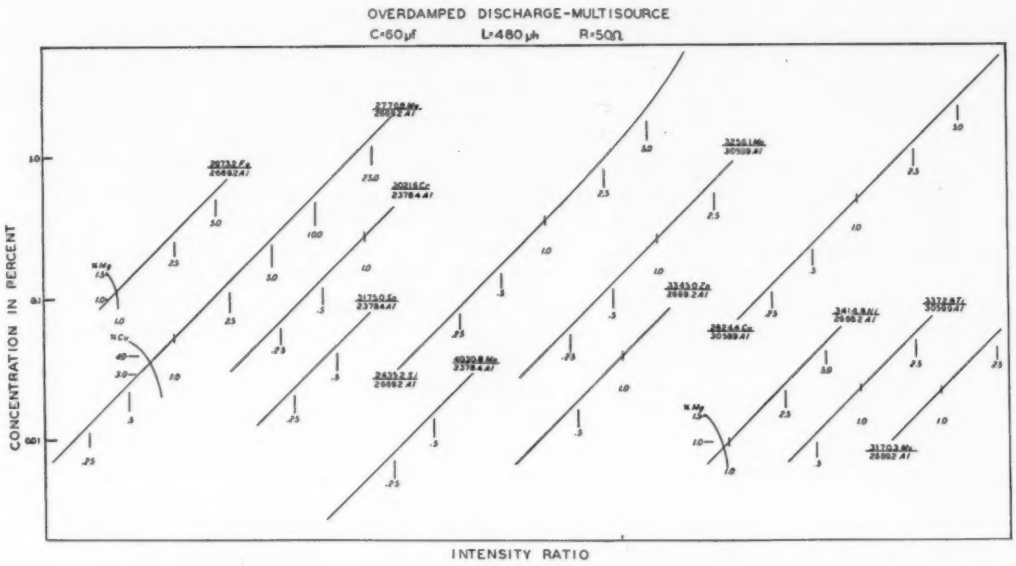

FIG. 3.

TABLE V. Data for the analysis of aluminum alloys.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
			a. C=5 μf, L=480 μh, R=100 ohms.				
Cu	3274.0	0.01%	3274.0/3059.9	0.014 –0.092%		0.0345%	1.2%
			2961.2/3059.9	0.8 –5.3			
Si			2514.3/3059.9		0.045–4.0%	0.71	1.4
Mg	2852.1	0.001	2852.1/3059.9	0.004 –0.025		0.0076	
			2783.0/3059.9	0.22 –1.6		1.03	0.59
Mn			2949.2/3059.9	0.003 –0.06		0.06	0.72
			2688.2/3059.9	0.4 –1.1		0.87	
Fe	3020.6	0.05	2395.6/3059.9		0.08 –0.42	0.163	1.7
Cr	4254.3	0.008	2822.4/3059.9	0.011 –0.044		0.0385	1.2
Sn	3175.1	0.02	3175.0/3059.9	0.02 –0.1			
Zn	3345.0	0.04					
Ni	3414.8	0.02	3414.8/3059.9	0.01 –0.064			0.66
Mo	3170.3	0.02	3170.3/3059.9	0.0072–0.053		0.047	2.8
Ti	3372.8	0.007	3372.8/3059.9	0.0072–0.054			1.3
			b. C=60 μf, L=480 μh, R=50 ohms.				
Cu	3247.5	0.0002%	2824.4/3059.9	0.072 –5.0%		0.52%	1.8%
Si	2881.6	0.0005	2435.2/2669.2	0.032 –0.8	0.8 –6.0%	0.36	1.8
Mg	2852.1	0.00007	2779.8/2669.2	0.007 –2.0		0.052	3.4
Mn	4030.8	0.0007	4030.8/2378.4	0.0027–0.032		0.032	2.1
			3256.1/3059.9	0.028 –1.0		0.26	
Fe	3020.6	0.002	2973.2/2669.2	0.086 –0.72		0.116	1.2
Cr			3021.6/2378.4	0.031 –0.46		0.278	1.8
Sn	3175.0	0.001	3175.0/2378.4	0.013 –0.084			
Zn	3345.0	0.002	3345.0/2669.2	0.007 –0.088		0.04	2.1
Ni	3414.8	0.0004	3414.8/2669.2	0.007 –0.065		0.0099	2.7
Mo	3170.3	0.001	3170.2/2669.2	0.01 –0.062		0.0225	2.1
Ti	3372.8	0.001	3372.8/3059.9	0.007 –0.078		0.0233	0.60
Pb	2833.1	0.003					

* Percent at which the intensity ratio of the line pair given is equal to one.

TABLE VI. Data for the analysis of magnesium alloys.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
			a. C=5 μf, L=100 μh, R=10 ohms.				
Al			2652.5/3074.0	3.4 –14.5%		12.5%	1.2%
Zn			3282.3/3329.9	0.72 – 4.2			0.66
Mn	4030.8	0.01%	2949.2/3329.9	0.067 – 0.46		0.153	1.6
Cu	3274.0	0.002	3274.0/3329.9	0.015 –0.11		0.079	1.1
Si	2881.6	0.03	2881.6/3329.9	0.029 – 0.1			
Ni	3414.8	0.007					
			b. C=60 μf, L=480 μh, R=50 ohms.				
Al			2652.5/3074.0	3.6 –14.5%**		12.3%	1.6%
Zn			3282.3/3074.0	0.63 – 5.8		1.03	1.8
Mn			3228.1/3074.0	0.063 –0.59		0.455	3.1
Cu			3274.0/3074.0	0.018 – 0.074			2.5
Si	2881.6	0.02%	2881.6/3074.0	0.019 – 0.073			3.6
Ni	3414.8	0.002	3414.8/3074.0	0.0025– 0.008			
Fe	3020.6	0.001	3020.6/3074.0	0.0064– 0.033			1.7
	2395.6	0.001					

* Percent at which the intensity ratio of the line pair given is equal to one.
** Linear but not at 45°. See Fig. 4 and text.

TABLE VII. Data for the analysis of zinc alloys.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
			a. C=5 μf, L=480 μh, R=100 ohms.				
Al			2660.4/3018.4	3.0 –7.4%			1.2%
Cu	3274.0	0.01%	3274.0/3018.4	0.12 –0.47			
			2961.2/3018.4	1.6 –3.3			1.1
Fe	2395.6	0.01	2395.6/3018.4		0.014–0.094%		3.9
Mg	2852.1	0.002	2790.8/3018.4	0.023 –0.076		0.034%	2.3
Mn			2949.2/3058.8				0.87
			b. C=60 μf, L=480 μh, R=50 ohms.				
Al			3059.9/2542.3	3.5 –4.5%			2.2%
Cu			2961.2/2542.3	0.2 –1.3			1.3
			2882.9/2542.3	1.0 –3.5		1.56%	
Pb	2833.1	0.0006%	2833.1/2670.5	0.002 –0.025		0.195	1.1
Fe	3020.6	0.0007	2994.4/2542.3		0.014–0.07%	0.0285	2.3
Mg	2852.1	0.0002	2783.0/2542.3	0.025 –0.07		0.0485	1.1
Cd	2288.0	0.0002	2288.0/2542.3	0.0015–0.003			2.0
Sn	3175.1	0.0005	3175.1/2542.3			0.00102	2.0

* Percent at which the intensity ratio of the line pair given is equal to one.

the elements cannot be measured to as low concentrations in this "b" case as compared to the "a" case.

The third case is definitely arc-like, the findings being presented in Table IVc. This represents results obtained with a counter electrode of carbon with circuit conditions identical with those used in the self-electrode case down in Table IIIa. The effect of the carbon counter electrode is to make the discharge definitely more spark-like with a consequent reduction of sensitivity on many of the arc lines.

The next system investigated is that of aluminum alloys, using the Petrey stand technique. The standards used were a set obtained from the Aluminum Company of America, including high copper and magnesium standards. Table V gives data for the analysis of aluminum alloys using a spark-like (Table Va) and an arc-like (Table Vb) source. Here again precision is sacrificed for sensitivity in the arc-like case. However, the sensitivity obtained in the Vb case is truly remarkable, while the precision is still sufficient for control analysis, testifying to the versatility of the multisource unit.

Figure 3 shows working curves for the arc-like

case. Here again wide ranges of concentration are covered with little or no self-absorption. However, another analytical difficulty is encountered, the influence of one element on another. This source has very high sensitivity, a fair degree of precision, and can be used for a wide range of concentrations. High magnesium, however, influences the analysis of iron and nickel, and high copper that of magnesium. The type of correction used here is a plot of concentration of interfering element *versus* shift of the index point of the working curve necessary to give a correct analysis. When slide-rule types of calculators are used, the correction curve is projected along with the working curve. Then, instead of the rule being set to the normal index point at an intensity ratio of one, it is set at a point on the correction curve corresponding to the concentration of the interfering element present. When the working curve is used "as is," the correction curve represents the figure by which the result obtained from the working curve must be multiplied to give the correct result. For example, in an aluminum alloy containing 1.5 percent magnesium, the result obtained for nickel from the working curve must be multiplied by 0.705 to give the correct result. With the increasing complexity of alloys and the high degree of standardization required for routine analytical laboratories, this type of correction should be given more attention than it has had in the past.[6] It is certainly less cumbersome than determining and using a different set of working curves for every type of alloy, particularly in a laboratory handling a large variety of alloys.

The third system is that of magnesium alloys. The standards used were a set obtained from the Aluminum Company of America. Table VI gives the analytical data for a spark-like (Table VIa) and an arc-like (Table VIb) case. Working curves for the arc-like case show no self-absorption (Fig. 4), and demonstrate the wide range of concentrations for which this source can be used; nickel being of the order of a few thousandths of a percent and aluminum around 10 percent. Aluminum gives a curve that does not conform to any of the theoretical curves. A satisfactory explanation for this has not been found, but the results are probably due to the changing physical properties of the alloy with changing aluminum concentration. Only the aluminum analysis is affected, and the change in slope is such that the precision of the determination of aluminum concentration is greater than the precision of the ratio of line intensities.

Data on an arc-like case for zinc using raised 60° cones on the surface of the disks are given in Table VIIb. This is the ideal case for zinc die-casting analysis which is still largely being done by spectrographic methods ten or more years old. With this new method determination of lead down to 0.0006 percent, cadmium to 0.0002 percent, and tin to 0.0005 percent proves very

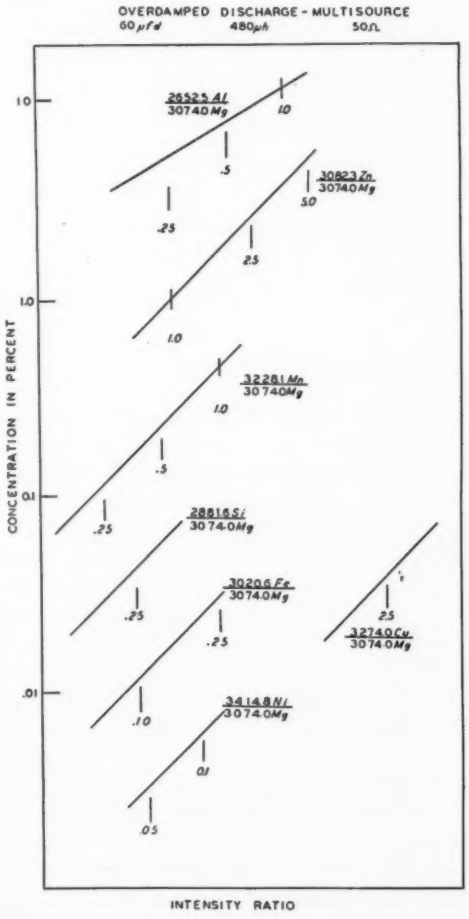

FIG. 4.

[6] M. F. Hasler, C. E. Harvey, and H. W. Dietert, Ind. Eng. Chem. Anal. Ed. **15**, 102–7 (1943).

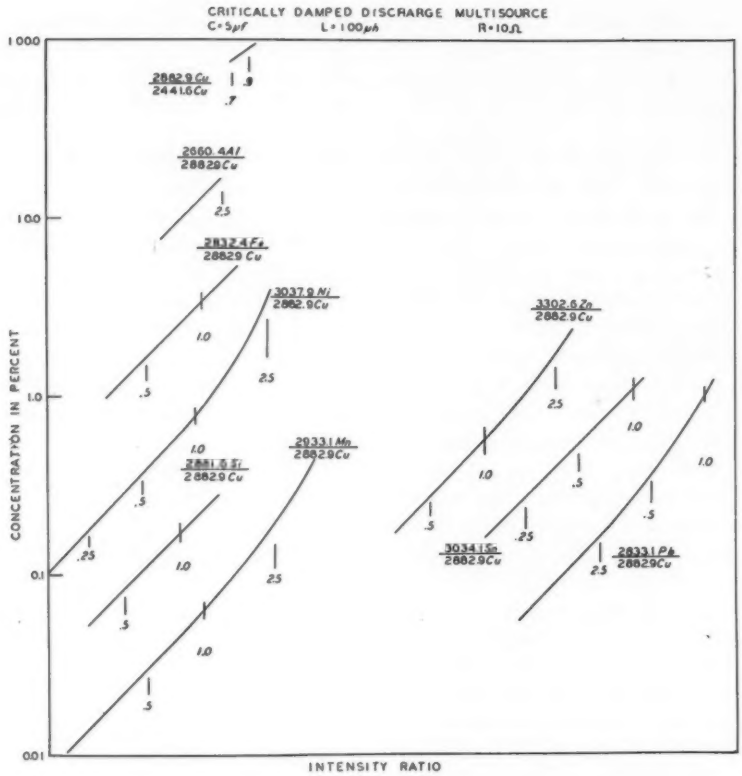

FIG. 5.

TABLE VIII. Data for the analysis of aluminum bronze.

$C = 5\ \mu f$, $L = 100\ \mu h$, $R = 10$ ohms.

	Sensitivity (I =0.3 background)		Line pair	Range: Working curve linear at 45°	Range: Working curve self-absorbed	Index point*	Precision (% average deviation)
Cu			2882.9/2441.6	75.0 –95.0%**			1.8%
Al			2660.4/2882.9	7.4 –17.0			0.50
Fe			2832.4/2882.9	1.0 – 5.5		3.45%	1.0
Ni	3414.8	0.02%	3037.9/2882.9		0.1 –4.0%	0.77	0.83
Zn	3345.0	0.02	3302.6/2882.9		0.17 –2.4	0.56	0.82
Pb	2833.1	0.04	2833.1/2882.9		0.055–1.3	0.95	1.9
Sn	3175.1	0.04	3034.1/2882.9	0.16 –1.3		1.08	1.4
Mn	4030.8	0.005	2933.1/2882.9	0.01 – 0.06	0.06 –0.46	0.061	0.63
Si	2881.6	0.001	2881.6/2882.9	0.051– 0.29		0.172	1.8

		Transmission readings (%)								Av. dev. of I
Mn	2933.1	28.8	28.0	29.8	28.3	28.8	28.5	28.9	29.0	1.1%
Cu	3010.8	34.8	34.4	35.8	34.3	34.4	34.1	34.3	34.3	0.94
		Intensity ratios								Av. dev.
$\frac{I2933.1\ Mn}{I3010.8\ Cu}$		1.19	1.21	1.19	1.19	1.18	1.19	1.18	1.17	0.01

* Percent at which the intensity ratio of the line pair given is equal to one.
** Linear but not at 45°. See Fig. 6.

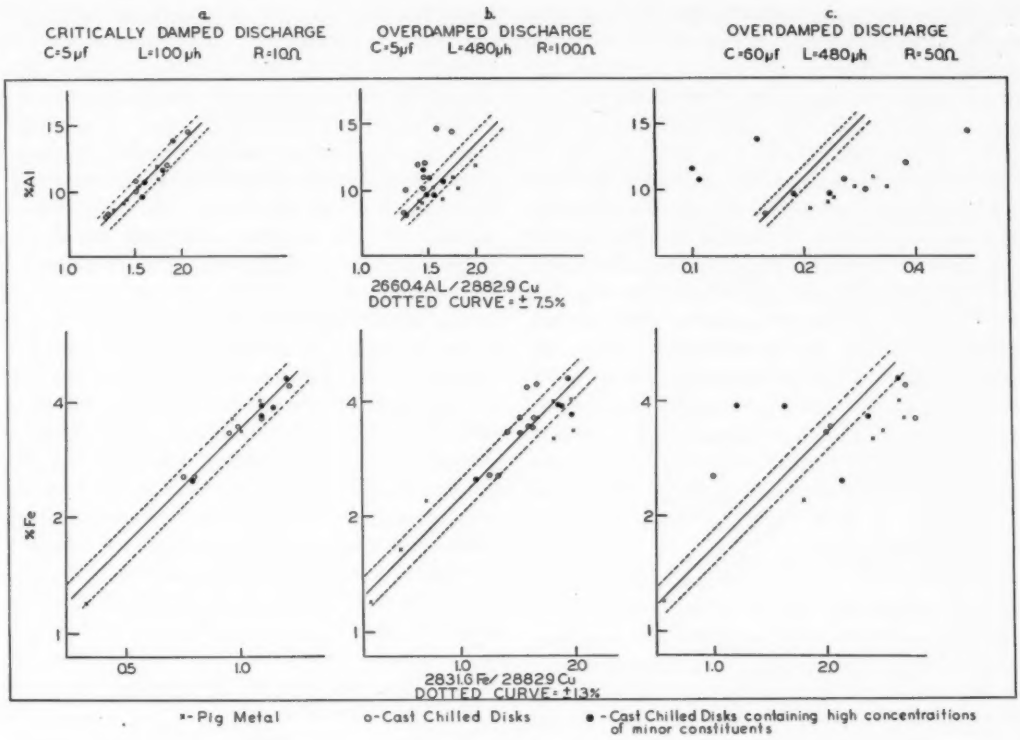

FIG. 6.

easy. This can be done simultaneously with the precise determination of aluminum at 4 percent, copper at 3 percent, and magnesium and iron at several hundredths of a percent. A spark-like case of less interest is shown in VIIa.

A spark-like case for aluminum bronze (Table VIII—Fig. 5) shows a very high degree of precision. An example of the reproducibility of repeat runs is given here. The two rows of figures near the bottom of the table are actual densitometer readings for copper and manganese lines on this run. The transmission readings were converted to intensities, and the average deviation from the mean is given in the last column. The degree of absolute reproducibility is remarkable, demonstrating the excellence of discharge control in the multisource. Calculated intensity ratios are given in the last row. Referring to the top of the table, note that copper can be determined with considerable accuracy by means of the ratio of two copper lines; although the copper is the principal constituent, ranging from 75 to 90 percent in this alloy. We feel that this type of analysis of major constituents will become increasingly popular, particularly after the effect has been studied under various excitation conditions with the multisource.

In setting up working curves for aluminum bronze analysis, an important analytical difficulty was encountered, one that is not often recognized. A large number of samples of this alloy were made available to us through the cooperation of Ampco Metal, Inc. These samples could be divided into three classes: aluminum bronze pigs, cast chilled disks of about the same composition as the pigs, and cast chilled disks having somewhat higher concentrations of minor constituents. The first spark-like case studied (Table VIII), of very high precision, gave working curves for aluminum and iron with a spread of points as indicated in Fig. 6a. It can be seen that the points for the three types

of samples are fairly well distributed about the curve. This discharge deposited considerable amounts of carbon on the sample electrode, the circuit constants being somewhat similar to those used on steel where the same phenomenon was noted. In the second case (Fig. 6b), one that is, incidentally, more spark-like than the first, the types of samples are no longer distributed about the curve in a random fashion. In the case of aluminum, two curves, neither of them 45°, could be drawn through the points, one for pigs and one for disks. The same is true for iron, but not quite so obviously. In the arc-like case (Fig. 6c), the situation has gotten completely out of hand. A curve could be drawn for aluminum similar to the one obtained in the magnesium arc-like case (Fig. 4), but would leave three points entirely unaccounted for. A curve could be drawn for iron in the pigs, but nothing could be done with the chilled disks.

There are certain points that should be made clear in discussing this situation. In all cases, the reproducibility of a single sample is better than the figure represented by the dotted curves. In the second case (Fig. 6b), for instance, the average deviation for aluminum is 1.7 percent and for iron 1.1 percent. Also, in none of the cases can the scattered points be corrected by setting up correction curves for one or two elements, as was done in the aluminum arc-like case (Fig. 3). Though the correct chemical analysis of aluminum bronze is very difficult, we believe that the original chemical analyses of the standards used were at least as good as the spread indicated in 6a.

Our interpretation of the situation is this—the metallurgical form of the sample is certainly significant in the analysis of certain complex alloys.[4] In the first case, the discharge conditions which deposit a carbon layer on the sample appear to allow correct analyses independent of the different metallurgical histories of the samples. In the second case (Fig. 6b) the results on the pigs are self-consistent, as are those on disks, but they each give different working curves. In the arc-like case (Fig. 6a) the pigs are still consistent, but minor variations in the metallurgy of the disks make it impossible to analyze them with this type of source. It appears that some, but not all, of these variations are due to variations in composition. The effect of varying several constituents is so complex, however, that correction curves cannot be used conveniently. As previously mentioned, the way to solve the problem is to choose a source that will eliminate these effects. Making a choice between an arc or a spark will not solve the problem except accidentally. In working with iron, aluminum, magnesium, and zinc, no significant difference between the two spark-like cases studied was found. With aluminum bronze, however, having a special critically damped spark case available represents the difference between success and possible failure. We feel that by carrying these studies further, it will be possible to devise a system of analysis suitable for both major and minor constituents in most brasses and bronzes. Obviously, to do this, a source unit making available a wide range of discharge conditions is necessary. It is worthy of note that the multisource unit offers approximately 500,000 separate controlled sources to choose from.

To summarize, the multisource makes available to the analyst an instrument with the following advantages:

1. Spark-like sources with moderate sensitivity and precision equal to or greater than the standard high voltage spark units now available.

2. Arc-like sources with high sensitivity, precision approaching that of spark sources, and very little self-absorption, making it possible to cover very wide ranges of concentrations accurately.

3. A wide variety of intermediate sources making it possible to effect a reasonable compromise between sensitivity and precision in the solution of any given problem; and making it possible to solve difficult problems arising from the effect of one element on another, differences in metallurgical history of samples, etc.

In this report we have investigated the spectrographic analysis, with the multisource, of various alloys of iron, aluminum, magnesium, zinc, and copper-aluminum. In each case practical working conditions were found which in general represent improvements over those obtainable with conventional arcs or sparks. We plan to extend this survey to other alloys and non-metallic materials at a later date.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 1 JANUARY, 1944

The Use of Briquets Formed from Metal Grindings for the Spectrographic Analysis of Steel*

R. E. NUSBAUM, D. L. FRY, AND J. W. HACKETT
Research Laboratories Division, General Motors Corporation, Detroit, Michigan

IN many cases samples of a given alloy are submitted for spectrographic analysis in a wide variety of shapes and sizes. In order to adapt these analyses most effectively to a routine process, it is necessary to have a method of sampling which can be applied generally to all such samples. One of the most promising sampling methods for this purpose is that in which briquets, made from the material to be analyzed, are used as electrodes in the arc or spark. This paper describes a spectrographic analysis technique, involving the use of briquets, which has been under development for the last year or so, and which has recently been applied in steel and cast iron analyses.

The general use of briquets for spectrographic analysis has been the subject of one paper[1] in the literature and the use of "pressed pellets" for the analysis of nickel alloys has been described in another.[2] As far as is known there has been no satisfactory procedure for making briquets from all types of iron alloys.

PARTICLE SIZE

In order to examine the effect of the size of the particles in the briquet upon the reproducibility of the spectrographic analyses of the briquets, particles from a sample of cast iron were obtained. Three groups of particles were selected, namely, particles between the mesh sizes of 60 to 100, 100 to 200, and 200 to 300. A number of briquets were formed from each group, and these were sparked. The reproducibility of the logarithms of intensity ratios for different particle sizes were compared on charts such as that shown in Fig. 1. These are data for manganese in a sample of cast iron. It can be seen that for all five prespark times the smallest particles gave somewhat better reproducibility than did the larger ones. This was found to be true for both manganese and silicon, and the effect was consistently observed for all samples examined. It seems reasonable to assume that the better reproducibility of analyses obtained for small particles is associated with the fact that more compact briquets can be formed when the particles are small. Another reason for reducing the sample to relatively fine particles is the fact that better sampling is obtained. This is especially desirable in materials where there may be segregation. In order to compromise between requirements of speed and particle size a 150-mesh screen has been used for most of the work.

METHOD OF OBTAINING FINE PARTICLES

In order to make the use of briquets a practical sampling method for iron alloys, it is necessary to have a means of rapidly obtaining fine particles from alloys of wide degrees of hardness. In the attempt to satisfy these requirements various cutting tools such as drills, rotary files, and special milling tools, some of which have been described in the literature, were tried. It was found, however, that the process of using these tools was too slow for the problems concerned; in the case of the harder alloys it was practically impossible. The method found to be the most satisfactory was that of grinding. With the proper selection of wheels, metals of widely different degrees of hardness could be ground, and small particles could be obtained rapidly. The grinders used for this work are small bench models and are easily obtained.

After the grindings are obtained they are screened, and the large particles are discarded.

In the analyses of these briquets there are two sources of error which are directly associated with the grinding process. One is the burning of particles in grinding, and the other is the contamination of the sample by particles of grinding wheel. Burning of the metal is greatly suppressed by using the softest wheels possible and holding the sample against the wheel with a very light force. The same treatment of all samples of each alloy

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] Harry W. Dietert, J. Opt. Soc. Am. **31**, 693 (1941).

[2] C. J. Neuhaus, J. Opt. Soc. Am. **33**, 167 (1943).

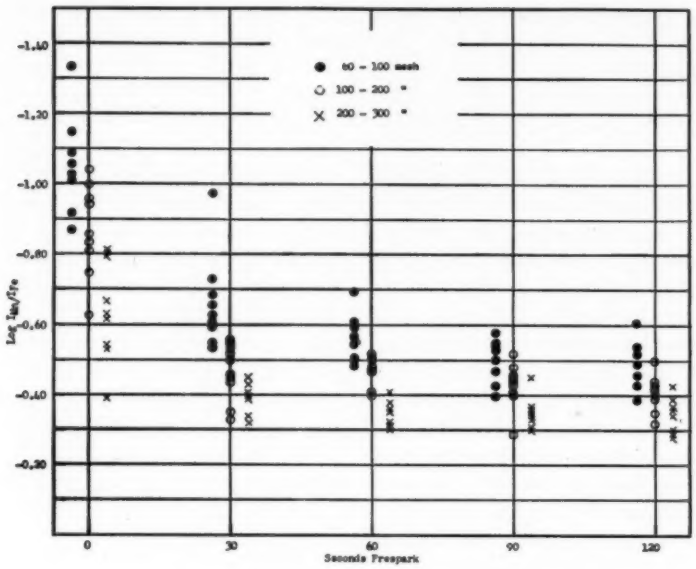

FIG. 1. Relationship between reproducibility and particle size.

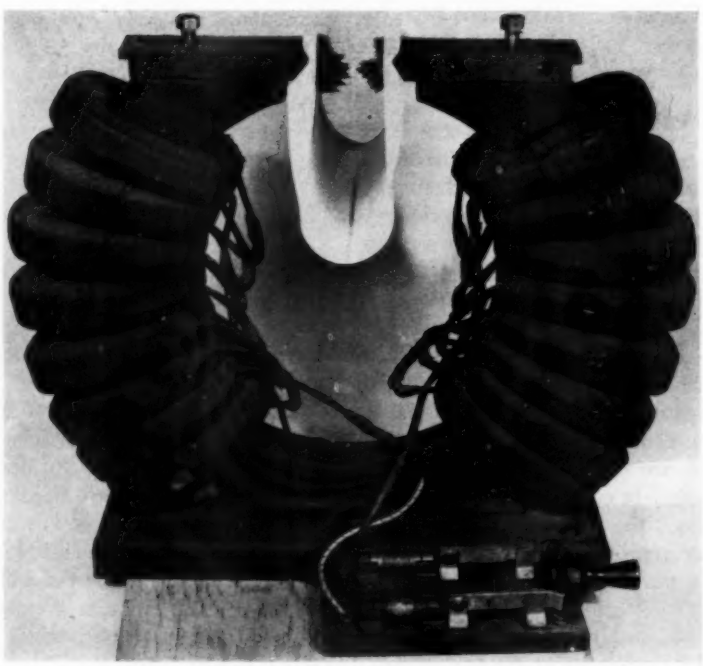

FIG. 2. The magnetic separator.

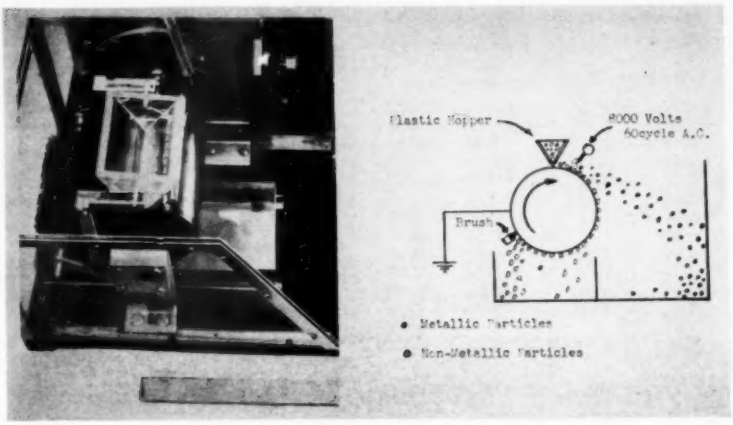

FIG. 3. Picture and diagram of the electrostatic separator.

is assured by using the same grinding wheel and grinding technique. Two steps are taken to minimize errors due to contamination of the sample by grinding-wheel particles. First, grinding wheels, in which the abrasive and the bonding material contain as little as possible of the elements sought in the analyses, are selected. For the applications described in this paper, analyses are made for manganese, silicon, chromium, and molybdenum. The grinding wheels used in these cases are Alundum wheels with either vitrified or resinoid bonds. The only metals present in these wheels in any appreciable quantity are aluminum and magnesium. However, other kinds of wheels, such as boron carbide, could be used if necessary. Second, two methods are used for removing stone particles from the grindings. After the grindings have been screened, the fine particles are put through a process which separates the grinding-wheel particles from the metal to be analyzed. A magnetic method is used for samples which can be magnetized, and an electrostatic method is used for those materials which cannot be magnetized.

Figure 2 shows an electromagnet which is used for the magnetic separation. The magnet is operated on 110 volts d.c. and gives a field of 20,000 gauss with an air gap of one inch. This is a stronger field than is needed for most samples. The particles to be separated are placed on a sheet of tough paper; the paper is then folded to form a trough and is placed between the poles of the magnet as shown in Fig. 2. The particles are agitated by moving the paper back and forth in a sawing motion, causing the stone particles to fall to the bottom of the trough. About one minute was found to be time enough for adequate separation.

During the development of the process three examinations were made regularly to determine the degree of separation which was accomplished. The cleaned material was examined with a binocular microscope, and both qualitative spectrographic and quantitative chemical analyses were made before and after briquets were formed. These examinations showed that the separations were good but not perfect. However, it was found that the number of stone particles was reduced to a point where they did not affect the analyses in question; that is, the analysis of cast iron for manganese and silicon, and two steels for the four elements, manganese, silicon, chromium, and molybdenum.

When briquetted samples are to be used for the analysis of metals or alloys which cannot be magnetized, such as stainless steel containing 18 percent chromium and 8 percent nickel, an electrostatic separator shown in Fig. 3 is used to separate wheel particles from the metal. This separator consists of a copper-surfaced drum, 4 inches in diameter and 4 inches long, and rotating at 300 r.p.m., a plastic hopper from which the grindings are fed onto the grounded drum surface, and some metal points at approximately 8000 volts

TABLE I. Effect of Al_2O_3 in briquets on log I ratio.

Sample No.	Wheel used	Number of times through separator	Chemical analyses Silicon	Al_2O_3	Log I ratios Mn	Si
5565	20L	0	0.40%	12.65%	−0.34	−0.82
5565	20L	2	0.39	3.45	−0.38	−1.05
5565	20L	4	0.42	2.54	−0.40	−1.10
5565	20L	6	0.43	2.16	−0.44	−1.15
5312	46Q	0	0.55	4.34	−0.51	−0.70
5312	46Q	1	0.47	1.72	−0.55	−0.75
5312	46Q	2	0.59	1.22	−0.56	−0.76
5312	46Q	3	0.51	1.07	−0.56	−0.75
5312	46Q	4	0.51	0.95	−0.54	−0.70
5312	46Q	8	0.55	0.81	−0.57	−0.70

TABLE II. Optimum conditions for spectrographic analyses of briquets.

Metal to be analyzed	Resistance in discharge circuit	Prespark in seconds	Exposure in seconds
Cast iron	27 ohms	10	30
18–8	18 ohms	5	45
Mod. S.A.E. 4150	18 ohms	5	40
S.A.E. 1020	18 ohms	5	90

For all metals: Secondary voltage 30,000, no inductance added in discharge circuit, capacity 0.015 μf, spark gap $\frac{1}{2}$ inch, and air jet pressure 1 lb. per square inch behind jet, diameter of the jet $\frac{1}{8}$ inch.

TABLE III. Spectrum lines used for analyses.

Metal to be analyzed	Int. Std. iron line	Manganese	Silicon	Chromium	Molybdenum
Cast iron	2880.76*	2933.06	2881.58		
18–8	2523.66	2558.59	2516.12		
S.A.E. 4150	2885.93	2886.68	2881.58	2867.65	2816.15
S.A.E. 1020	2885.93	2886.68	2881.58	2867.65	2816.15

* All wave-lengths are in international angstrom units.

60 cycle. A corona discharge at the metal points causes the particles to become charged as they are carried around by the drum. The electrically conducting, metal particles are thrown from the drum into one tray while the non-conducting grinding-wheel particles stick to the drum and, after being carried through about three-fourths of a revolution, are brushed into a second tray. Successful operation of the unit depends upon having the proper relationship between speed of rotation of the drum, and the potential and orientation of the metal points. The separator works best when the range of particle sizes is not too great.

The metal particles and stone particles are not perfectly separated by being put through the separator once. In the case of 18-8 steel this is explained, to some extent at least, by the fact that there is a tendency for the two kinds of particles to stick together. Table I shows the results of making successive separations on two samples of this steel. These observations show that (1) the amount of Al_2O_3 present depends upon the type of grinding wheel used, (2) the Al_2O_3 content is reduced rapidly at first and then somewhat more slowly, (3) the amount of silicon added by the Al_2O_3 is negligible compared to the 0.4 or 0.5 percent present in this particular steel, and (4) there is little or no effect on the log I ratios for either manganese or silicon if the amount of Al_2O_3 is less than about three percent. (In order to insure this degree of separation the samples are regularly put through the separator six times.) It should be pointed out that these data refer only to electrostatic separations. The experience in this work indicates that magnetic separation is more definite, and is, therefore, to be preferred when a choice of methods is possible.

FORMING THE BRIQUET

Two percent of high purity carbon is thoroughly mixed with the metal particles before they are pressed into briquets. The carbon lubricates the wall of the die and thereby facilitates the removal of the briquet. The use of fine particles and the addition of the small amount of carbon make it unnecessary to use excessively high pressures. This simplifies the requirements of the press and increases the life of the die. A few observations have indicated that the manganese and silicon log I ratios are not altered by the addition of carbon. A force of 8000 pounds applied to $\frac{1}{4}$-inch diameter plunger is regularly used in forming the briquet. A variation in the force of 25 percent does not affect the analyses of the briquets. In order to produce briquets with the same density at each end, the die is operated in a press in such a way that plungers at both ends are free to move during the pressing operation. The briquets used in this work are $\frac{1}{4}$ inch in diameter and about $\frac{3}{8}$ inch long. They weigh about 1.5 grams. A cone of 140° included angle is ground on the end of each briquet before it is sparked.

The time necessary for one man to prepare briquets from a solid sample was 20 minutes when magnetic separation was used, and 25 minutes when electrostatic separation was used.

TABLE IV. Summary of briquet analyses data.

(1) Type of sample	(2) No. of samples	(3) No. of determinations	(4) Ranges of concentrations	(5) Average deviation from mean	(6) Maximum deviation from mean	(7) Standard deviation	(8) Av. dev. of chemical from analytical curve
			Manganese				
Cast iron	6	101	0.50%–1.30%	1.8%	7.4%	2.42%	3.4%
18–8 steel	8	168	0.60 –1.80	1.8	9.3	2.34	1.5
Mod. S.A.E. 4150 steel	20	115	0.80 –1.30	1.0	4.5	1.41	3.8
			Silicon				
Cast iron	6	101	1.20 –2.60	3.5	10.7	4.45	2.9
18–8 steel	8	168	0.40 –0.60	2.6	12.2	3.48	5.9
Mod. S.A.E. 4150 steel	20	115	0.30 –0.60	3.4	12.5	4.67	9.5
			Chromium				
Mod. S.A.E. 4150 steel	17	90	0.30 –1.00	2.3	11.0	3.02	6.4
			Molybdenum				
Mod. S.A.E. 4150 steel	15	84	0.10 –0.40	2.7	13.6	3.75	9.2

SPECTROGRAPHIC ANALYSES OF THE BRIQUETS

The spectrum is excited with a controlled, condensed spark circuit. The condenser is charged in the usual way with a transformer; the discharge circuit contains a rotating gap, a resistance, inductance, and capacitance. An air jet is directed toward the spark gap. Briquets of the sample to be analyzed are used for both the upper and lower electrodes. The thermal capacity of the spark stand, which is relatively small, is the only source of cooling of the briquets during the sparking. Circuit constants, air-jet pressure, prespark time, exposure times, and gap length used are shown in Table II.

The spectrograph used for this work is a double Cornu prism instrument which was constructed in our laboratory and has not yet been described in the literature. Spectra are recorded on Eastman Spectrum Analysis No. 1 plates. The plates are calibrated by means of a rotating log sector disk with a d.c. arc as a light source. A Hilger microphotometer is used for determining line intensity ratios from the photographed spectra.

Analytical curves have been established for the determination of manganese and silicon in cast iron and 18-8 stainless steel; and for manganese, silicon, chromium, and molybdenum in a modified S.A.E. 4150 steel. The spectrum lines used are shown in Table III. The same internal standard line has been used for all elements determined in each alloy.

TABLE V. Standard deviations for S.A.E. 1020 steel.

Manganese	2.41%
Silicon	3.63
Chromium	2.33
Molybdenum	3.71

Standard deviations of some spectrographic analyses of briquets of three iron alloys are shown in column 7 of Table IV. Column 2 gives the number of samples analyzed in each case, and column 3 the total number of determinations. For example, six samples of cast iron were analyzed for manganese and silicon, and each analysis was repeated about sixteen times making a total of 101 determinations for each of the two elements. Column 6 gives the maximum deviation from the mean. Of the 101 analyses of cast iron for manganese one determination differed from the mean by 7.4 percent. The data in Table IV represent work which was in progress for some months. Therefore, the deviations include any variations in the measurements of log I ratios caused by possible day-to-day changes in the electrical constants of the circuit, or other parts of the procedure. Every determination made in this series of analyses of these alloys is included.

The average deviations of the chemical analyses from the analytical curves are shown in column 8. All samples referred to in the table were used to establish analytical curves, and the curves were drawn to fit all samples as well as possible.

The briquet sampling method has also been used for the semi-quantitative analyses of some S.A.E. 1020 steel samples. In this case only relative concentrations of manganese, silicon, chro-

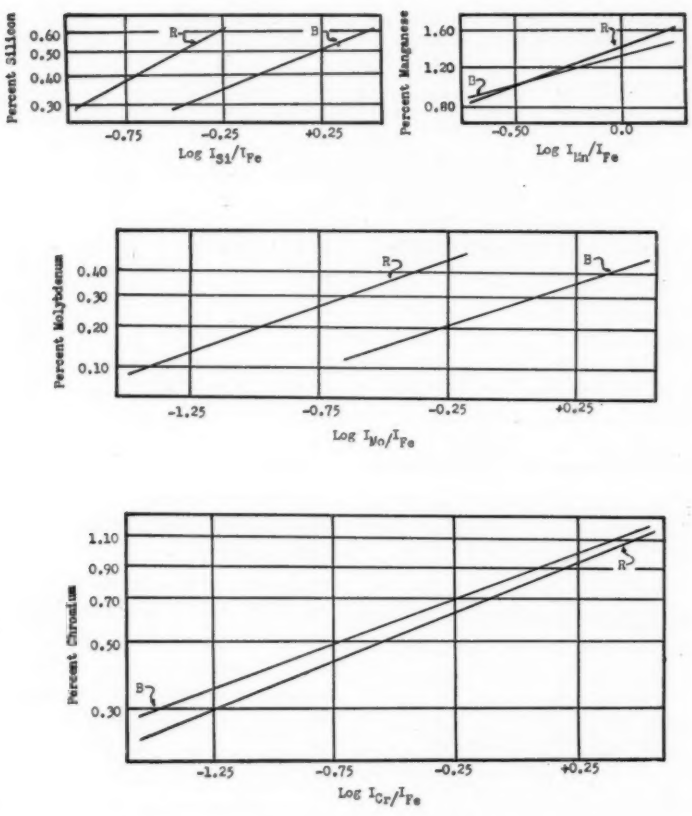

FIG. 4. Analytical curves for modified S.A.E. 4150 steel.

mium, and molybdenum in different samples were determined. No chemical analyses were made on these samples, and, for this reason, no analytical curves for this alloy could be established. In order to determine relative concentrations, extensions of the curves for S.A.E. 4150 were used. Two analyses were made on each of twenty samples, and the percent deviation of each analysis from the mean of the two was determined. The standard deviation for the group was obtained for each element, and these values are shown in Table V. This table shows that the relative values for different samples of this steel are determined about as accurately as are the analyses for the other alloys discussed, indicating that the briquet method is equally applicable to 1020 steel.

COMPARISON OF BRIQUETS AND RODS

The general method of using briquetted samples has been examined by comparing analyses of these samples with those of rod samples. Although analytical curves for the two cases would not necessarily be expected to be the same, it was interesting to compare them. Figure 4 shows this comparison for modified S.A.E. 4150 steel. It should be pointed out that for both rods and briquets the spark circuit, exposure conditions, and spectrum lines used were identical. It will be noted that the analytical curves for silicon and molybdenum in briquets are shifted toward higher values of positive log I ratios, while the curve for chromium is shifted in the opposite direction, and that for manganese is almost identical for the two types of sampling. In the case

TABLE VI. Summary of rod analyses data.

(1) Type of sample	(2) No. of samples	(3) No. of determinations	(4) Range of concentrations	(5) Average deviation from mean	(6) Maximum deviation from mean	(7) Standard deviation	(8) Av. dev. of chemical from analytical curves
			Manganese				
18–8 steel	10	109	0.60%–1.80%	2.1%	6.0%	2.61%	2.8%
Mod. S.A.E. 4150 steel	43	100	0.85 –1.55	1.7	5.1	2.20	4.4
			Silicon				
18–8 steel	10	109	0.35 –0.65	3.6	12.9	4.73	7.6
Mod. S.A.E. 4150 steel	43	100	0.30 –0.65	3.6	14.3	5.12	10.3
			Chromium				
Mod. S.A.E. 4150 steel	28	71	0.25 –1.05	1.5	8.1	2.40	5.5
			Molybdenum				
Mod. S.A.E. 4150 steel	19	47	0.150 –0.320	1.5	5.8	2.09	4.5

of silicon and molybdenum it might indicate that these elements are being added in the briquetting process. There are, however, two important pieces of evidence to the contrary; (1) chemical analyses do not show an addition of silicon and the addition of Al_2O_3 up to as high as 12 percent does not cause very great changes in the silicon log I ratios, and (2) it was found that there was a similar shift in the analytical curve for briquets, even when the briquets were formed from particles obtained by milling.

The most significant information gained from the comparison of briquets and rods has come from the comparison of actual analyses (obtained by using the appropriate analytical curve) of both forms of sample. Some samples of 18-8 and 4150 steel were analyzed both as briquets and as rods. The data on rods are summarized in Table VI. Tables IV and VI give the same information about the two different types of sampling. These data show that the standard deviations of the spectrographic analyses of briquetted samples compare very favorably with those of the analyses of cast pins or rods. It is to be expected then, that essentially the same accuracy can be obtained whether the sample be briquetted or analyzed as a rod.

TABLE VII. Spectrographic analyses of mixtures.

Element analyzed for	Analyses of components *A*	*B*	Calculated analysis of mixture $1/2A + 1/2B$	Number of observations	Average spectrographic analysis of mixture	Average deviation from calculated analysis
Manganese	1.07%	0.36%	0.72%	7	0.70%	3.3%
Silicon	2.15	2.62	2.38	7	2.37	5.1

SUPPRESSION OF EFFECTS OF SEGREGATION

One of the original reasons for working with briquets was the fact that it was believed briquetting would suppress errors due to segregation. To test this possibility two samples with widely different manganese and somewhat different silicon concentrations were ground up and mixed together in equal proportions. The results of analyses of the mixture are shown in Table VII.

The average percent differences between the actual spectrographic analyses and the calculated analyses are comparable to the average percent deviation from the mean obtained for non-mixtures. Since this is so, the analysis, which one would expect from a briquet made from a sample containing segregation, would represent the true average analysis of the part of the sample converted to fine particles. It should be pointed out, however, that this suppression of errors due to segregation can be realized only when the briquet is made of particles which are small compared to the volume of the material vaporized in the spark.

PREPARATION OF A SERIES OF STANDARDS

The briquetting method furnishes a means of obtaining a series of standards from two samples of known concentrations. To show this, grindings from a sample of cast iron were diluted with grindings from Armco iron. The results of the spectrographic analyses of these mixtures are shown in Table VIII. The average percent deviations from the calculated values are again comparable to the average percent deviation from the mean for non-mixtures. Therefore, as these

TABLE VIII. Spectrographic analyses of prepared standards.

Samples mixed	Analysis of components E-5	Armco	Calculated analysis of mixture	Number of observations	Average spectrographic analysis of mixture	Max. dev. from calculated	Av. dev. from calculated
			Manganese				
75% E-5+Armco	1.21%	0.43%	1.02%	4	1.08%	6.9%	6.1%
50% E-5+Armco	1.21	0.43	0.81	4	0.80	6.2	3.1
			Silicon				
75% E-5+Armco	2.62	0.04	1.97	4	1.96	5.1	2.8
50% E-5+Armco	2.62	0.04	1.33	4	1.26	7.5	5.6

data show, it is possible to obtain one cast iron sample with large amounts of silicon and manganese, and from it prepare a series of standards representing a total range of concentrations. This method of obtaining standards can probably be extended to other types of alloy.

Another possible application of this mixing process would be its use for the determination of components appearing in relatively high concentrations. The grindings from the sample could be mixed in a definite proportion with grindings from another sample of a similar alloy containing a known low concentration of the elements in question.

SUMMARY

One-fourth-inch briquets are formed from particles, smaller than 150 mesh, obtained by grinding a portion of the sample with a suitable grinding wheel. The grinding-wheel particles are separated from the metal grindings by either a magnetic or an electrostatic separator. Two percent of carbon is added, and the particles are then pressed into a briquet with a pressure of 163,000 pounds per square inch.

Samples of cast iron, and 18-8 steel have been analyzed for manganese and silicon, and samples of a modified S.A.E. 4150 steel and S.A.E. 1020 steel have been analyzed for the four elements manganese, silicon, chromium, and molybdenum. In all cases standard deviations of the spectrographic analyses of briquets are comparable to those ordinarily realized for the spectrographic analyses of rods.

The method as it has been used here has these advantages: (1) It is a general sampling method for iron alloys. That is, briquets can be made from samples having nearly any shape or size; they can be made from samples which are not easily kept in solution, and from materials which are too hard to machine readily. (2) Since fine particles can readily be obtained, the method tends to suppress errors due to segregation. These errors are difficult to avoid in ordinary rod sampling methods. (3) The method can be conveniently adapted to the preparation of a series of standard samples.

The Spectrographic Flat Surface Sparking Technique of Steel Analysis*

CHARLES L. GUETTEL
Rock Island Arsenal Laboratory, Rock Island, Illinois

WHEN the present Rock Island Arsenal spectrographic equipment was installed in March, 1940, the initial plan for the quantitative analysis of steel specimens, which were received in a variety of shapes and forms, was to core drill or machine two metallic "pins" from each sample, and use the "pins" as electrodes in conjunction with a high voltage controlled spark. Although calibration curves based on such a technique were prepared, it was soon found that due to the lengthy time of electrode preparation the method did not justify its use in preference to wet analysis. A more rapid and simple method of electrode preparation was necessary in order for the spectrograph to compete with the other forms of analytical techniques of steel analysis.

The simplest method brought verbally to the attention of the Rock Island Arsenal Laboratory was the flat surface sparking technique used by the Aluminum Company of America for the analysis of aluminum alloys. This method since has been published.[1] No literature written in the United States appeared to be available at the time concerning the application of such a method to steel analysis, although it was learned after adopting the technique to routine work in May, 1940, that F. G. Barker of the Admiralty Laboratory, Sheffield, England, had reported on such a technique in early 1939.[2] In view of the fact that the technique has been given little publicity in this country, and since control laboratory methods of spectrographic iron and steel analysis have over-shadowed the techniques of the testing laboratory, it appears that a report on the procedure would be appropriate.

Although the Arsenal laboratory is now modernizing its spectrographic equipment to improve further the application of the flat surface technique, the satisfaction obtained by the method for over three years, with the equipment on hand, encourages the writer to publicize the basic idea of the technique to others in war work at this time, rather than to wait for further experimentation with new equipment that as yet has not been installed completely.

For the original calibration the standards used were steel specimens, which had been saved over a period of a year, in order to obtain points on the curves representing the extreme limits of the concentration ranges desired. Chips of these standards had been analyzed in duplicate by wet analysis and checked against steels from the Bureau of Standards. The comparison of preliminary results between the spectrographic and wet methods were encouraging and soon, enough confidence was established to use the flat surface sparking technique as a routine tool in steel analysis.

THE EQUIPMENT

The ARL-Dietert Spectrograph used in the Arsenal laboratory is a grating instrument having an original concave diffraction grating with 24,000 lines per inch.[3] The grating has a linear dispersion of 7A per mm in the first order and may resolve lines 0.1 to 0.2A apart in the wavelength region of 2380A to 4600A, the spectral region to which the Arsenal instrument is adjusted permanently.

The circuit of the ARL-Dietert a.c. spark source used in the steel analysis includes a controlled spark based on a sychronous gap in the secondary circuit.[3] A 2-kva oil insulated transformer supplies 35,000 volts peak from 115 volts a.c. mains. Primary power is regulated with a tapped choke through a selector switch. The same switch controls the secondary capacitance, putting 1, 2, or 4 condenser plates into the circuit, the plates being protected from breakdown by air cooling provided by a blower built into the unit. An automatic timer is incorporated into the unit to regulate the time of excitation.

The film comparator is a dual projector with

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] H. V. Churchill and J. R. Churchill, J. Opt. Soc. Am. **31**, 611 (1941).

[2] F. G. Barker, J. Iron and Steel Inst. **139**, 228 (1939).

[3] *Spectrochemical Analysis* (Applied Research Laboratories, Glendale, California), commercial publication.

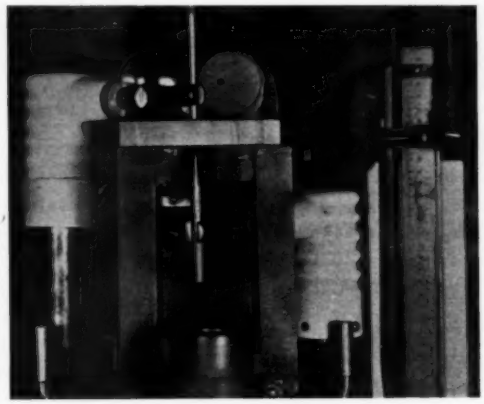

FIG. 1. Sample support on spark stand showing lower carbon electrode.

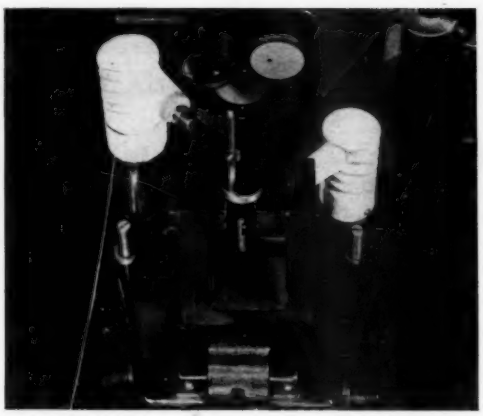

FIG. 2. Sample support on spark stand showing direction of air blast to sample.

the sample film projected on the upper portion of a 24″×30″ screen and a master plate on the lower portion.[3] Approximately 1 cm of the 32-cm spectrogram is projected at one time. The master plate covers the wave-length range obtained with the ultraviolet position of the slit, 2380–4600A. On the master plate are included a wave-length scale on which from two to four of the most persistent lines of approximately 70 elements are shown and labeled. A projected dispersion of 0.11A per mm is obtained which is ample to define the finest details that can be resolved by the grating.

The densitometer consists of a pick-up amplifier assembly and the control meter.[3] The former is mounted on a faceplate that is fastened into the projection head of the comparator and consists of a light pick-up device containing a 0.0005″ slit, drive mechanism with motor, photo-cell, and amplifier tube. A voltage compensator is connected to the circuit to eliminate the effect of line voltage fluctuations on the readings.

The developing equipment consists of commercial apparatus which includes a rocking developing machine, a film washer, and a film dryer incorporating an infra-red lamp and blast of air.

ANALYTICAL PROCEDURE

In routine, the flat surface of the steel specimen is polished on a sanded polishing wheel. To regulate the size of the analytical spark gap to obtain the highest accuracy, a surface grinder is used occasionally to insure a flat surface for excitation. The specimen, with its polished surface down and serving as one electrode, is bridged across two wooden supports, $\frac{3}{4}$″ apart, standing on the arc-spark stand base.

The specimen is connected to the upper electrode clip of the arc-spark stand by means of a wire or small steel rod. The upper clip may be moved sideways to accommodate higher specimens mounted on the supports. Between the supports and held in the lower electrode clip, is the lower carbon electrode which has been sharpened to a point in a pencil sharpener. The tip of the carbon has been flattened to a $\frac{1}{32}$″ diameter by means of a file and special fixture. (A motor-driven electrode cutter now is being adopted for this purpose.) The spark gap between the flat surface of the specimen and the pointed carbon is held at $\frac{3}{32}$″. The gap is determined for the upper electrode by the constant height of the support stand (see Fig. 1). The location of the lower pointed electrode is determined by the position of the image of the electrode on the frosted glass viewing lens of the arc-spark stand. A distance of 50 cm separates the analytical gap from the slit.

An air blast blown into the analytical gap and recorded relatively but exactly at 20 mm of Hg pressure by a manometer on the open system (equivalent to approximately 12 pounds pressure when the system is closed) and controlled by a valve is used in conjunction with the spark

excitation. The source of the air blast is a $\frac{1}{4}''$ diameter glass tube mounted on the side of the optical bench in front of the arc-spark stand with the orifice $3\frac{3}{4}''$ from the analytical gap (see Fig. 2). The air is cleansed and dried before its release into the gap by circulating through a Binks oil and water trap, and air dryer filled with silica gel.

The maximum power, secondary capacitance, and inductance attainable from the spark unit are used. These values, according to the manufacturer, are 2 kva, 0.014 microfarad, and 0.32 millihenry, respectively. The actual voltage across the analytical gap is unknown but is held relatively constant at a value of "40" on the panel meter during excitation. The input voltage to the unit is controlled to 110 volts. Each sample is presparked for 15 seconds before the optical path shutter is opened and then exposed for 15 seconds. The slit width is 65 microns. No lenses are used anywhere in the optical system.

The carbons used for the lower pointed electrodes are "Spectroscopic Carbons," manufactured by the National Carbon Company. The use of a carbon electrode introduces cyanogen bands but the bands appear in spectral regions not used in the analysis.

The spark strikes an area of approximately $\frac{3}{16}''$ to $\frac{1}{4}''$ in diameter on the steel surface. Under the influence of the air blast, this area is increased to approximately $\frac{1}{2}''\times\frac{3}{8}''$ as shown by the oxidized surface after excitation.

The film used is Eastman Spectrum Analysis No. 2, 35-mm film. (Eastman Spectrum Analysis No. 1 film gives higher contrast, slightly better resolution, and more rapid fixing, but its sensitivity above 3900A is extremely low.) Each film may contain as high as 10 spectrograms. The film is extracted from the camera with a film removal case and developed in a diluted Eastman D-8 developer (one part of stock solution to one part of water). The developing time is exactly 45 seconds at a temperature of 70°F. The developer is stored in six-ounce bottles to prevent oxidation. A fresh developer solution is used daily. After development, the film is placed in an acetic acid

TABLE I. Element and internal standard lines.*

Element line	Internal standard	Concentration ranges (%)
Mn 4034.490	Fe 4118.549	Mn 0–1.50
Cr 4289.721	Fe 4282.406	Cr 0–1.30
Ni 3050.819	Fe 3083.742	Ni 0.20–3.50
Si 2881.578	Fe 2941.343	Si 0.10–1.00
Si 2881.578	Fe 2880.756	Si 1.70–2.25
Mo 3170.347	Fe 3205.400	Mo 0–1.00
V 3093.108	Fe 3091.578	V 0–0.30
Al 3944.032	Fe 3906.482	Al 0.10–1.30
Cu 3273.962	Fe 3286.755	Cu 0–0.80
Zr 3273.047	Fe 3271.002	Zr 0–0.20

* Wave-lengths as given by G. R. Harrison, *Massachusetts Institute of Technology Wavelength Tables* (John Wiley and Sons, New York, 1939).

TABLE II. Excitation and developing conditions.

Source	a.c. spark
Upper electrode	Steel specimen
Lower electrode	Pointed carbon
Lower electrode tip	Flattened to $\frac{1}{32}''$ diameter
Spark gap	$\frac{3}{16}''$
Power	2 kva
Secondary capacitance	0.014 microfarad
Inductance	0.32 millihenry
Input voltage	110 volts
Output voltage (relative)	"40" on panel
Prespark	15 seconds
Exposure time	15 seconds
Distance of electrode gap from slit	50 cm
Slit width	65 microns
Air blast pressure	20 cm Hg (on manometer—open system)
Developer	Eastman D-8 (one part stock solution, one part water)
Acetic acid rinse bath	Eastman SB-1a (one part glacial acetic acid, eight parts water)
Fixer	Standard x-ray fixer
Developing time	45 seconds
Developing temperature	70°F

TABLE III. Comparison of chemical and spectrographic results on manganese and chromium in steel.

Type of steel	Chemical (%)	Spectrographic (%)[a]
S.A.E. 3140	Mn 0.73, 0.74	Mn 0.74
4140	Mn 0.72, 0.73	Mn 0.73
6150	Mn 0.77, 0.77	Mn 0.78
6150	[b]Mn 0.707	Mn 0.70
4130	Mn 0.60	Mn 0.59, 0.61
4130	Mn 0.56	Mn 0.56, 0.57
4130	Mn 0.57	Mn 0.59, 0.58
4130	Mn 0.73	Mn 0.80, 0.76
3140	Cr 0.61, 0.61	Cr 0.64
4140	Cr 1.05, 1.08	Cr 1.01
6150	Cr 1.02, 1.04	Cr 0.98
6150	[b]Cr 0.977	Cr 0.99
4130	Cr 0.67	Cr 0.68, 0.70
4130	Cr 0.65	Cr 0.65, 0.67
4130	Cr 0.65, 0.66	Cr 0.66, 0.65
4130	Cr 0.64	Cr 0.67, 0.64

[a] These results were obtained under the best conditions possible. All spectrographic samples were ground smooth on the surface grinder. All samples were sparked in the same direction in relation to the surface marks from the surface grinder. Assurance was made that no part of the specimen interfered with the air blast before the air reached the analytical gap.

[b] Sample and analysis from the Bureau of Standards.

rinse bath for 10 seconds. It is fixed in standard x-ray fixing solution, remaining in the latter for about one minute after clearing, dried in the dryer from 3 to 5 minutes, and is then ready for densitometer readings.

For each roll of film, a film characteristic or gamma-curve is plotted. In order to determine the film characteristic curve, a stepped sector operating in conjunction with a slit in the secondary source plane provides four adjacent spectra $\frac{1}{16}''$ in height, having intensities of 1, $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{8}$, respectively. The desired curve may then be obtained by plotting the log transmission of the four steps against the log of the given intensities. The stepped sector is on the periphery of a rotating disk. The source of illumination is a 500-watt tungsten filament Mazda CX lamp (G.E.) exposed six minutes during the rotation of the stepped sector with the quartz lens in the optical path. In practice, transmission readings are taken at 3500, 3510, 3520, 3530, 3540, 3550A on each of the four steps. The readings are averaged to obtain the transmission value of each step. The four given intensity values then are plotted on the calculating board as abscissae against the transmission values as ordinates, both on log scales. The intensity values used in establishing the analytical curves are obtained from transmission values converted to actual intensities through the film characteristic curve. As in most standard practices, the working analytical curves in the form of individual concentration scales are substituted for the intensity ratio on the abscissa to read directly in percentage. No effort is made to correct for the negligible background.

DISCUSSION

The elements determined quantitatively are given in Table I with analytical ranges and wavelengths of lines used. A summary of excitation and developing conditions is given in Table II.

An idea of the accuracy obtainable under careful control may be noted by a study of Table III where the chemical and spectrographic results for manganese and chromium are compared. (Manganese and chromium are the elements most frequently determined spectrographically in the Arsenal laboratory.) The usual precision in a series of trials run within ± 5 percent of the mean results when the trials are run off within a short period of time. The day-to-day accuracy using the present excitation equipment shows a variation which necessitates careful checks with standard samples to determine possible shifting of the analytical curves. This variation has been found to be due to the effects of changing humidity on open condenser plates. During periods of high humidity the spectrograms were underexposed, necessitating longer exposures or the use of the curved portion of the film characteristic curve, checking with standard samples in either case, to compensate for the humidity effects. The laboratory is confident that the equipment now being installed and to be mentioned below will correct the latter adverse effects.

The accuracy may be affected by heterogeneity of the sample, an effect which can be diminished by averaging two or more results on the same specimen.

Variations in specimen size do not introduce any noticeable effects unless the sample is extremely small. Small specimens, the size of a coin or thin strip stock, give erratic results due to lack of heat dissipation which, in turn, varies the nature of the spark. If desired, special calibration curves could most likely be established to cover small specimens cut to a definite size.

Slight surface variations obtained with the polishing wheel do not appear to influence the intensity ratios.

Since the variety of heat treatment in specimens spectrographically tested showed no noticeable effect on analytical results, it has been assumed that the effect of physical condition is negligible. Barker also reports that the physical condition of the steel does not affect the result.[4]

It was found that the nature of the spark reached a period of greater stability after a short presparking period. This conclusion was reached from a study of the intensity ratios plotted against time. A 15-second prespark is included also in the procedure to "burn off" possible contamination from handling or from the sanded polishing wheel and to assure an improved thermal equilibrium in the spark by using a "warm-up" period. The air blast, besides break-

[4] F. G. Barker, J. Iron and Steel Inst. **139**, 240 (1939).

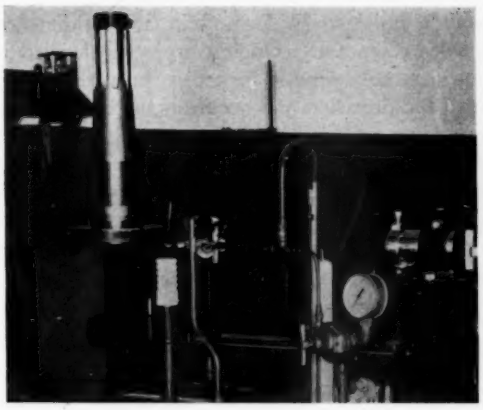

FIG. 3. Mounting of shaft to determine type of steel.

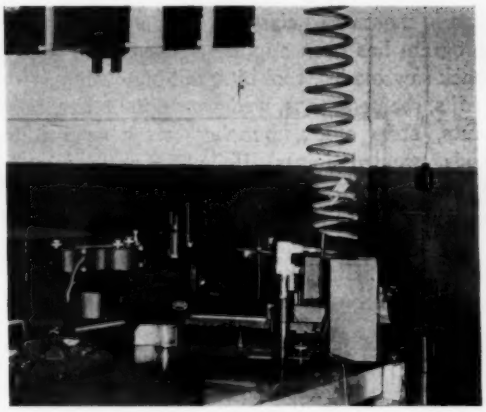

FIG. 4. Mounting of large spring to determine type of steel.

ing off the oscillations before the discharge becomes arc-like in character,[5] helps the spark to reach a more stable thermal condition through the cooling effect, preventing any excessive rise in temperature as the excitation proceeds.

The effect of extraneous elements on the analytical curves of other elements in the steel has been noted definitely in the case of aluminum in Nitralloy steels where the entire spectrogram is underexposed. The aluminum oxide formed most likely interferes with the usual characteristics of the spark. To determine manganese, chromium, silicon, and molybdenum in Nitralloy steels, special analytical curves for this type of steel would have to be established.

Molybdenum steel standards, ranging from 0.21 to 0.80 percent molybdenum and representing eight different types of steel, produced calibration points that followed one analytical curve. The data indicated that the molybdenum determination was not affected by the variety of other elements in these standards.

Spectrographic manganese and chromium determinations also appear not to be influenced by the presence of nickel, molybdenum, and vanadium in three common types of steel. Chromium and manganese results were checked against the wet analysis on a 3140 (Cr-Ni) steel, a 4140 (Cr-Mo) steel, and a 6150 (Cr-V) steel. Using the same chromium and manganese analytical curves for all three steels in the spectrographic determinations, the two independent methods checked within 0 to 4 percent of one another regardless of the extraneous presence of nickel, molybdenum, or vanadium in the specimens.

Manganese results tend to go approximately 10 percent high in steels containing 2 percent silicon or thereabouts. Either a separate calibration curve for manganese in silicon steels must be prepared or a correction factor, experimentally determined, must be applied to the original manganese working curve.

Manganese in high manganese tool steels and in high sulfur containing steels (S.A.E. X13— series) cannot be determined from the same manganese working curve due to the extraneous effect of the sulfur on the manganese—iron intensity ratios.

Although a complete investigation of the effects of all extraneous elements on the analytical curves has not been made, the agreement between the wet method and the spectrographic technique appears to show that the magnitude of any other such effect is less than the random errors involved.

If only the type of steel rather than a complete quantitative analysis is desired, it is not necessary for the surface of the specimen to be flat nor the specimen destroyed. Any means of mounting the specimen is satisfactory provided the analytical gap is located properly. By merely checking the projection of the film without resorting to densitometer readings, an experienced observer

[5] R. A. Sawyer and H. B. Vincent, *Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications* (John Wiley & Sons, New York, 1938), p. 1.

can in most cases classify the type of steel. This program has been applied to specimens such as hack-saw blades, tool bits, milling cutters, twist drills, reamers, taps, wedges, engine parts, bolts, nuts, strip stock, punches, washers, welding rods, welded joints, Belleville springs, scrap turnings, shop machine parts, roller and ball bearings, wires, hammers, wrenches, pliers, miscellaneous test bars, castings, forgings, and many other variety of samples which are daily occurrences in a routine testing laboratory.

A distinct advantage of the flat surface sparking technique is the ability to analyze extremely large specimens. If the sample is too heavy for the support stand or the optical bench, an auxiliary stand mounted adjacent to the optical bench on the spectrograph table (see Figs. 3 and 4) or jacks standing on the floor next to the arc-spark stand are used to support the specimen across the optical path.

After the installation of the new equipment which will include a new commercial multi-source unit[6] to be located in a humidity-controlled room and a modern projector-densitometer, a more thorough investigation will be made into the precision and accuracy of the technique including more experimentation with effects such as spark gap distance, presparking, air blast pressure, specimen size and surface, heterogeneity, and extraneous elements. It is expected that the present technique will have to be modified slightly for the new equipment.

SUMMARY

A spectrographic, routine testing laboratory method of steel analysis involving a flat surface sparking technique is presented.

ACKNOWLEDGMENT

The writer is indebted to members of the staff of this laboratory for their constructive criticisms.

[6] M. F. Hasler and H. W. Dietert, J. Opt. Soc. Am. **33**, 4 (1943).

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 34, NUMBER 1 JANUARY, 1944

Geometric Formulation of Classical Color Harmony*

PARRY MOON, *Massachusetts Institute of Technology, Cambridge, Massachusetts*

AND

DOMINA EBERLE SPENCER, *Tufts College, Medford, Massachusetts*

1. INTRODUCTION

SINCE the time of Leonardo da Vinci—and undoubtedly before—every artist appears to have formulated his own system of color harmony. Many of these systems are interesting, some of them have elements of merit, but none gives a comprehensive scientific treatment. By a process of trial and error, an artist finds a few harmonious relations of colors which he uses over and over again with slight modifications. Yet each artist seems to feel that his pet system embraces the whole field of harmony and that any other system is worthless.

It must be emphasized that no scientific theory of color harmony is possible without a satisfactory method of color specification. And no such method was available until very recent years. Thus most of the speculations in the literature are necessarily vague and incomplete. It was not until 1931 that the C.I.E. method of color designation came into being,[1] and even this system in its original form is not suitable for work in color harmony because equal distances in C.I.E. space do not correspond to equal perceptual steps in color. Recently, however, the Munsell system (which is founded on equal perceptual steps) has been correlated with the C.I.E. system.[2] A metric

* Paper presented at the Twenty-Eighth Annual Meeting of the Optical Society of America, Pittsburgh, Pennsylvania, October 7–9, 1943.

[1] Commission Internationale de L'Eclairage, Compte rendu (1931).

[2] S. M. Newhall, D. Nickerson, and D. B. Judd, J. Opt. Soc. Am. **33**, 385 (1943).

colorspace has also been developed by mathematical transformation of the C.I.E. space.[3] Thus an adequate scientific foundation is now available for the first time, and a scientific theory of color harmony can now be produced.

The purpose of this paper is to present a scientific basis for a comprehensive theory of color harmony. It does not reject the previous theories of the artists[4] but combines them into an integrated whole. The basic principle behind all this work is that any arrangement of colors that can be sensed as an *orderly combination* will be pleasing. The general method is to reduce the problem to one of geometry in ω-space.[3] Various types of harmony correspond to various geometric figures in this space. Thus it is possible to list harmonies with reference to straight lines, triangles, circles, and other simple figures in ω-space. Tabulations are given which include the various special cases that have been advocated previously by Chevreul, Bezold, Brücke, Munsell, Ostwald, Birren, Graves, and others.

Classical color harmony ignores a number of factors that have important bearing on the subject. The effect of area is almost completely neglected. Adaptation of the eye is ignored. Also, some harmonies are more pleasing than others and a rating system is desirable but has never been developed. In the present paper, these limitations of classical theory remain and no attempt is made to do more than correlate the classical theories and present them in a more scientific form. In subsequent papers, however, the best relative areas for the colors will be considered, visual adaptation will be introduced, and the merits of various harmonies will be compared by means of *aesthetic measure*.

2. THE HISTORY OF COLOR HARMONY

The development of a theory of color harmony has had to wait on two advances: 1. The production of technical dyestuffs and pigments, 2. the invention of a suitable metric colorspace for the geometric specification of color.

Obviously, there could be no adequate color harmony as long as the available colorants were very limited in variety, nor could there be a quantitative theory until methods had appeared for the accurate specification of color. In ancient times only a few coloring materials were available, and pleasure was derived more from the intrinsic beauty and symbolic meaning of the colors than from their interrelations. In the middle ages, other pigments were discovered and painting was freed from some of the trammels of the past. Leonardo da Vinci was one of the first writers to mention the harmony of colors but his remarks are necessarily rather vague. In all the work in color harmony until comparatively recent times, the accent has been entirely on the *harmony of hues*. A famous book written in 1810 by Goethe[5] emphasizes this aspect. In fact, the popular idea even today is that harmony deals only with hue.

An extension was made by Chevreul[6] in his study of harmony. Apparently it was he who introduced the idea of classification into *harmonies of analogy* and *harmonies of contrast*. The analogy or contrast can be in terms of hue, brightness, or saturation. These ideas are included in practically all of the subsequent treatments of harmony but have been expressed only qualitatively.

Bezold (1874) and Brücke (1887) advanced the idea that nearby hues can be used together harmoniously, as can complementary and near-complementary hues. But there is an intermediate region where the effect is displeasing. With a 12-hue color circle a color difference less than 1 step is good, as are steps of more than $\frac{1}{3}$ of the circle; but intermediate differences are displeasing.

[3] P. Moon and D. E. Spencer, J. Opt. Soc. Am. **33**, 270 (1943).

[4] From the voluminous literature on the art of color, the following may be mentioned: Maitland Graves, *The Art of Color and Design* (McGraw-Hill, New York, 1941); Cyril Pearce, *Composition* (Scribner's Sons, London, 1927). A. W. Dow, *Composition* (Doubleday, Page and Company, New York, 1919); Walter Sargent, *The Enjoyment and Use of Color* (Scribner's Sons, New York, 1923); O. N. Rood, *Textbook of Color* (D. Appleton and Company, New York, 1916); Roland Rood, *Color and Light in Painting* (Columbia University Press, New York, 1941); C. G. Cutler and S. C. Pepper, *Modern Color* (Harvard University Press, Cambridge, 1923); E. N. Vanderpoel, *Color Problems* (Longmans, Green and Company, London, 1902); F. Birren, *Monument to Color* (New York, 1938); Strathmore Paper Company, *A Grammar of Color* (Mittineague, Massachusetts, 1921); O. J. Tonks, *Color Practice in Schools* (Winsor and Newton, London); E. Burris-Meyer, *Historical Color Guide* (William Helburn, New York, 1938); Hilaire Hiller, *Color Harmony and Pigments* (New York, 1942).

[5] J. W. von Goethe, *Farbenlehre* (Weimar, 1810).

[6] E. Chevreul, *De la Loi du Contraste Simultané des Couleurs* (Paris, 1889).

The importance of *area* in color harmony was first considered quantitatively in 1845 by Field.[7] He said that the areas must be adjusted so that the mixture of the colors on a rotating disk gives a neutral gray. The same idea was used subsequently by Munsell.[8] On the other hand, Bezold,[9] Brücke,[10] and others disagreed with Field, partly because of their inability to obtain the identical colors used by Field, and partly for more fundamental reasons. Ostwald[11] also makes brief mention of area and gives the qualitative rule that the greater the purity the smaller should be the area. The general idea of area balance seems to be a valid one, though Field grasped only the special case of balance about an achromatic color. There is no reason why the balance point should be limited to any particular class of colors. Birren[12] mentions applications in which a chromatic balance point is chosen to obtain a particular psychological effect.

The further development of color harmony required a systematic method of arranging colors. The color solids of Munsell and Ostwald were developed independently in America and in Germany. Ostwald's basic idea in color harmony is that any orderly arrangement is harmonious. Thus any orderly geometric arrangement in the color solid should constitute a harmony. Ostwald considers the simplest arrangements such as definite spacings on the neutral axis or parallel to it, or simple spacings parallel to the surface of his color solid. From these simplest harmonies, the artist can progress to an almost unlimited number of more complicated arrangements, none of which Ostwald prohibits. He considers, however, that the sense of color harmony is so poorly developed that one must educate himself to appreciate the more complicated color arrangements. The Ostwald ideas of harmony can be applied equally well to the Munsell color solid,[13] though this fact does not seem to be generally realized. Munsell himself gave very little specific information on harmony, though he did mention the balance of colors about a neutral or other point and the orderly arrangement in the color solid.

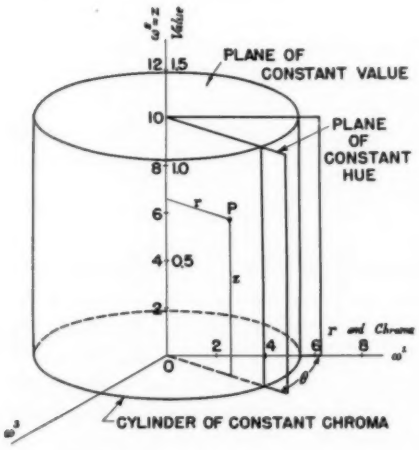

FIG. 1. The metric colorspace, showing the cartesian coordinate system $(\omega^1, \omega^2, \omega^3)$ and the cylindrical system (r, θ, z).

Thus technical developments in the production of colorants and progress in color theory have both helped in the advancement of color theory. There has been a real advance in the theory of color harmony, but this advance has been almost entirely qualitative. The Ostwald color solid still rests on a very insecure foundation, and it is only during the past five years that the Munsell system has been placed on a satisfactory scientific basis[2] with the aid of the C.I.E. system. So it is not strange that the vague ideas of the artist have not been translated into more scientific terms.

3. THE METRIC COLORSPACE

To make the theory of color harmony a branch of geometry, one must have first a metric colorspace. Such a space was developed for this purpose, as noted in a previous paper.[3] The C.I.E. specification of color gives an affine colorspace, where angles in general do not have any meaning and where distances in different directions cannot be compared. Such a space cannot be used for the geometrical formulation of color harmony until a metric is introduced. A Euclidean metric was

[7] George Field, *Chromatics* (London, 1845).
[8] A. H. Munsell, *A Color Notation* (Munsell Color Company, Baltimore, 1941).
[9] W. v. Bezold, *The Theory of Color* (American edition, Boston, 1876).
[10] E. Brücke, *Die Physiologie der Farben* (Leipzig, 1866); *Les Couleurs* (Paris, 1866).
[11] W. Ostwald, *Die Harmonie der Farben* (Leipzig, 1922); *Farbkunde* (Leipzig, 1923); *Color Science*, translated into English by J. S. Taylor (Vol. I, London, 1931; Vol. II, London, 1933).
[12] F. Birren, *Color Dimensions* (Crimson Press, Chicago, 1934).
[13] M. E. Bond and Dorothy Nickerson, J. Opt. Soc. Am. **32**, 709 (1942).

TABLE I. Desirable and ambiguous intervals between colors (ω space).

Pleasing interval	Displeasing interval	Variation in z only	Variation in r only+	Variation in θ only
Identity		0 to 1 j.n.d.	0 to 1 j.n.d.	0 to ±1 j.n.d.
Similarity	1st ambiguity	1 j.n.d. to 4*	1 j.n.d. to 3*	±1 j.n.d. to ±25°
		4 to 12	3 to 5	±25° to ±43°
Contrast	2nd ambiguity	12 to 20	5 to 7	±43° to ±100°
		20 to 80	7→	±100° to ±180°
	glare	>80	—	—

+ For simultaneous variation of z and r, see Figs. 3 and 4.
* Numbers refer to units of z or r in ω space.

TABLE II. Desirable and ambiguous intervals between colors (Munsell system).

Pleasing intervals	Displeasing intervals	Variation in value only	Variation in chroma only+	Variation in hue only
Identity		0 to 1 j.n.d.	0 to 1 j.n.d.	0 to 1 j.n.d.
Similarity	1st ambiguity	1 j.n.d. to ½ step	1 j.n.d. to 3 steps	1 j.n.d. to 7 steps*
		½ to 1½	3 to 5	7 to 12
Contrast	2nd ambiguity	1½ to 2½	5 to 7	±12 to ±28
		2½ to 10	7→	±28 to ±50
	glare	>10	—	—

+ For simultaneous variation of value and chroma, see Figs. 3 and 4.
* One hue step is equal to 1/100 of the complete hue circle.

developed to relate color steps to geometric distances.[3] The coefficients of the metric were determined in conformity with the latest Munsell data, and unit distance in any direction represents an equal color step.

The new metric space (ω space) is based on the general concept of the composite stimulus;[14] but in the present paper, simplicity is obtained by assuming constant visual adaptation to a neutral stimulus of Munsell value 5. This limitation allows a 1 : 1 correspondence between points in C.I.E. 3-space and in the metric ω space. Thus any given color, represented by (X, Y, Z) in the C.I.E. system, determines a unique point in ω space, a condition that would not obtain if adaptation were allowed to change.

The cartesian coordinate system is shown in Fig. 1, the three axes being designated as ω^1, ω^2, ω^3. Any color is represented by a point P. Brightness differences are measured in a direction parallel to the ω^2 axis. As is well known, however, hue is periodic and can be expressed best in terms of angles about the ω^2 axis. Thus it is convenient to employ a cylindrical coordinate system rather than a rectangular system. In cylindrical coordinates (r, θ, z),

$$\left.\begin{aligned}\omega^1 &= r\cos\theta\\ \omega^2 &= z\\ \omega^3 &= r\sin\theta.\end{aligned}\right\} \qquad (1)$$

Any colored light can be specified by (X, Y, Z). These coordinates can be transformed to (r, θ, z) and the color can be represented by a point in ω space. The theory of harmony of colored lights can be dealt with on this basis. The harmony of pigments can be handled in the same manner. Usually, however, it is more convenient to use Munsell notation. To a close approximation, z is found to be directly proportional to Munsell value, the unit of value being approximately 8 times the unit distance measured in the z direction.[15] Munsell chroma is measured radially and is approximately equal to r. Hue corresponds to the angle θ, the ten principal hues of the Munsell system being arranged at approximately equal angles about the z axis. It should be remembered[3] that the correspondence between ω space and the Munsell system is not perfect, though the approximation is ordinarily close enough so that color harmony examples can be

[14] D. E. Spencer, J. Opt. Soc. Am. **33**, 10 (1943).

[15] B. R. Bellamy and S. M. Newhall, J. Opt. Soc. Am. **32**, 465 (1942).

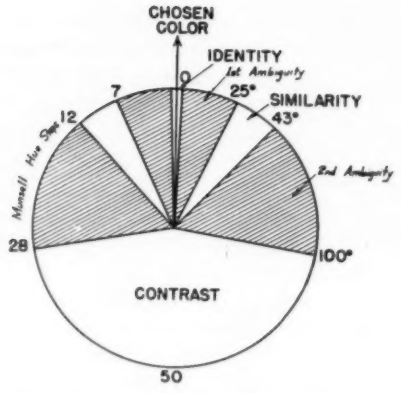

FIG. 2. Regions of similarity and contrast in a plane z=const. (constant Munsell value).

worked out in Munsell notation without direct use of the C.I.E. specification.

4. POSTULATES

Before attempting any new work in this field, one may ask himself, "What is color harmony?" The assumption, which is nowhere stated but which seems to be taken for granted throughout the literature, is that all color combinations can be divided into two distinct classes. These two classes are *harmonies* and *disharmonies*. There is supposed to be a perfectly sharp dividing line and every color combination must lie in one class or the other, all harmonies being equally pleasing and all disharmonies equally displeasing.

Probably the foregoing is an extreme statement of the usual tacit assumption, though it seems to be implied in the customary separation of a class of combinations called harmonies. Obviously the sharp division into two classes is not in accordance with fact. It seems likely that an artist can use any combination whatever, depending on the effect he wants to create: *There are no forbidden combinations, there is no division line.*

However, even after omitting such considerations as color associations, individual color preferences, and suitability to the application,[16] one finds that color combinations are by no means equally pleasing. In fact, they can be arranged in order of aesthetic merit, from combinations which expert and layman alike find very beautiful to combinations that no one likes. The purpose of color harmony theory is to provide a method of picking out color combinations that tend to rank high on this scale of aesthetic merit. These combinations may be called "harmonies," in deference to tradition, though they are not of equal merit and they do not constitute a definite class.

The theory of color harmony developed in this and subsequent papers rests on the following two postulates:

Pleasing combinations are obtained when

(1) the interval between any two colors is unambiguous, and when

(2) colors are so chosen that the points representing them in ω space are related in a simple geometric manner.

These postulates will now be explained. It is a fundamental principle of aesthetics that the observer should not be confused by the stimuli: there should never be a feeling of uncertainty. Applied to a variation in hue (or θ), the principle means that the hues should not be so close together that there is doubt as to whether they were intended to be identical or only similar. Another ambiguous region occurs between those hues which are definitely similar and those which are definitely dissimilar or complementary.

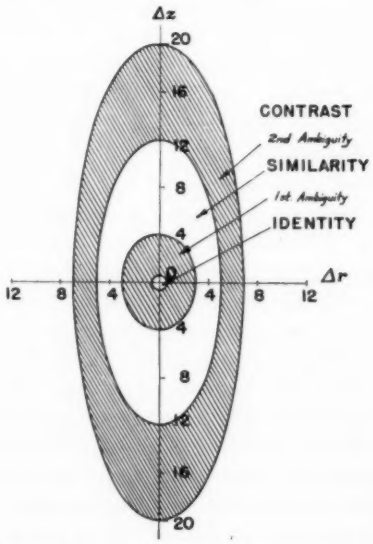

FIG. 3. Regions of similarity and contrast in a plane θ=const. (constant hue).

[16] E. C. Allen and J. P. Guilford, Am. J. Psychol. **48**, 643 (1936).

The same principle can be applied to other variations in color space. For example, ambiguous regions occur when there is variation in z alone, or in r alone. A study of the approximate limits of the various regions gives the results of Table I. A possible relation between two colors is obviously *identity*. This does not necessarily mean physical identity but merely indicates that the difference between two colors is less than one j.n.d. Other pleasing intervals give sensations of *similarity* or of *contrast*. Between identity and similarity and between similarity and contrast are regions of ambiguity.

The results of Table I for hue variations are shown graphically in Fig. 2. The diagram represents any plane z=const. and the numbers on the right are angles θ measured from an arbitrary color which is considered to be at 0° on the θ scale. Regions of ambiguity are cross-hatched. For example, if a red (Munsell 5 R) is the chosen color,[3] then 10 R and 10 RP are in the first ambiguous region while 10 YR, 5 Y, 10 Y, 10 PB, 5 P, 10 P are in the second ambiguous region. Preferred hues similar to 5 R are 5 YR and 5 RP, according to Fig. 2. For contrast 5 GY, 10 GY, 5 G, 10 G, 5 BG, 10 BG, 5 B, 10 B, 5 PB are satisfactory.

Table I shows that when there is a variation in z only, the colors appear similar if they differ by at least four and not more than twelve units in the z direction. When the difference is between

TABLE III. Ambiguity, similarity, and contrast in a plane of constant hue expressed in Munsell notation (see Fig. 4).

Region		Chroma difference	Value difference
	1st ambiguity	2	0
Similarity		0	1
		2	1
		4	0
	2nd ambiguity	0	2
		2	2
		4	1
		4	2
		6	1
		6	0
Contrast		0	3, 4, ··· 10
		2	3, 4, ··· 10
		4	3, 4, ··· 10
		6	2, 3, ··· 10
		8	0, 1, 2, ··· 10
	Glare	Any	>10

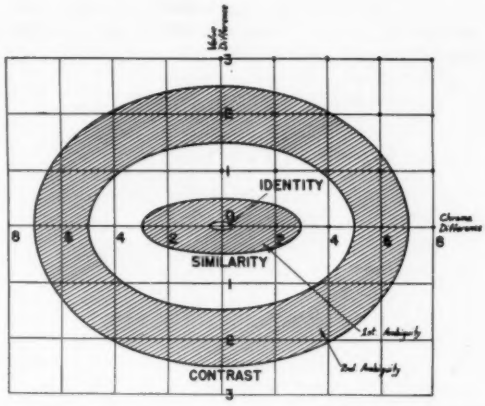

FIG. 4. Regions of similarity and contrast in a plane θ=const. (constant hue). Same as Fig. 3 but replotted in terms of Munsell value and chroma.

20 and 80 units in this direction a pleasant sense of contrast is found. Beyond approximately 80 units there is a tendency for an unpleasant effect of glare. Between the pleasing regions are intervals of ambiguity. The third column of Table I indicates similar limitations in the r direction. For example, take a color represented by the coordinates $z=10$, $r=5$, $\theta=0$. A pleasingly similar color could be any one of the following: $z=5$, $r=5$, $\theta=0$; $z=15$, $r=5$, $\theta=0$; $z=10$, $r=9$, $\theta=0$; $z=10$, $r=1$, $\theta=0$; $z=10$, $r=5$, $\theta=\pm 30°$.

Table II gives similar limits, expressed approximately in the Munsell system. It will be noted that the chroma limits are exactly the same as the variations in r of Table I. The "value" column, however, is different because the Munsell value steps are by no means equal perceptually to the chroma steps.[15] In both of these tables no attempt is made to specify the limits of the various regions in a highly precise manner. Lack of experience with accurately related colors has left most people with an undeveloped sense of color appreciation and it may even be doubtful that any amount of training will demand much more precise specifications than those given in the tables.

Tables I and II refer to one-dimensional variations. If r and z vary simultaneously, it is found that the previous tables are not directly applicable. What is needed is some kind of a map showing the preferred and ambiguous regions in the rz plane and reducing to the

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TABLE IV. Classification of harmonies.

Class I. One variable

1. Variable z
   - *A*. Achromatic
     - (*a*) Two color-points
     - (*b*) Three points
     - (*c*) More than three points
   - *B*. Chromatic
     - (*a*) Two points
     - (*b*) Three points
     - (*c*) More than three points
2. Variable r
   - (*a*) Two points
   - (*b*) Three points
   - (*c*) More than three points
3. Variable θ
   - (*a*) Two points
   - (*b*) Three points
   - (*c*) More than three points

Class II. Two variables

1. In a plane of constant θ
   - *A*. Points on a straight line
   - *B*. Triangles
   - *C*. Rectangles
   - *D*. Points on a circle
2. In a plane of constant z
   - (*a*) Two points
   - (*b*) Three points on isosceles triangle
   - (*c*) Five points on two triangles
   - (*d*) n points on a circle with center on neutral axis
   - (*e*) n points on a circle with center at a chromatic point
3. In a cylinder of constant r
   - (*a*) Two points
   - (*b*) n points on an ellipse with center on neutral axis

Class III. Three variables

1. With reference to planes of constant θ
2. With reference to planes of constant z
3. With reference to cylinders of constant r
4. With reference to tilted planes

tabulated values for the special cases of r=const. and z=const. Such a map is shown in Fig. 3. The transition points on the horizontal axis, representing variations in r only, are fixed by Table I at 3, 5, and 7. For the vertical axis, Table I fixes the points 4, 12, and 20. With simultaneous variation of r and z, preliminary experiments indicate that neither rectangular nor diamond-shaped areas are satisfactory but that ellipses may be used. Consequently, the regions of Fig. 3 are bounded by ellipses.

The same diagram is plotted in Munsell notation in Fig. 4. The only difference is a change in the vertical scale; the curves are ellipses as before. The black dots represent the colors given in any constant-hue chart of the *Munsell Book of Color*. A chosen color is considered at 0 of Fig. 4 and satisfactory colors for similarity and contrast are indicated by the dots. The results are summarized in Table III. For example, suppose the chosen color is *YR* 5/6. Then harmonies of analogy are obtained by use of any one of the colors *YR* 6/6, 4/6, 6/4, 6/8, 4/4, 4/8, 5/2, or 5/10 with *YR* 5/6. Contrast is obtained with *N* 2 or *N* 8, the other possible harmonies of contrast for this particular problem not being available in Munsell colors.

The two postulates are used together in building up a great variety of harmonies. The simplest arrangements employ straight lines in ω space and arrange the color points along a line with spacings that are simple multiples of each other. Points can also be arranged at the corners of a triangle or on a circle or ellipse; though, as Ostwald points out, there may be a question as to the degree of geometric complexity that can be recognized, at least without considerable further color education.

The basic aesthetic principle behind the second postulate is that pleasure is experienced by the recognition of *order*. Both aesthetic principles seem to be well established in a qualitative sense, and in this paper they are given quantitative significance. The idea of regions of ambiguity between regions of analogy and contrast was stated, though somewhat loosely, by Bezold[9] and by Brücke.[10] Chevreul[6] made extensive use of classification into harmonies of analogy and harmonies of contrast. Strangely enough, Ostwald[11] ignored this principle and based his work on the single maxim: *harmony equals order*. We have attempted to develop a system based on both principles.

5. CLASSIFICATION OF HARMONIES

A systematic classification of harmonies is given in Table IV. Since only three numbers are necessary for the specification of a color, it is obvious that all harmonies can be divided into three major classes. These have been called Class I, Class II, and Class III and they correspond to variations in one, two, and three dimensions, respectively.

Under Class I are the three subdivisions: variable z, variable r, and variable θ. With variation parallel to the z axis in ω space, there are two possibilities: the achromatic harmonies or harmonies of grays obtained by variation on the neutral axis, and the chromatic harmonies obtained by variation parallel to the z axis (change of Munsell value). Other harmonies can

be obtained by varying the radius r only (Munsell chroma) and by varying the angle θ about the neutral axis (Munsell hue). Each of these four classifications can be subdivided into two-color harmonies, three-color harmonies, and harmonies of more than three colors.

Class II contains all harmonies obtained by simultaneous variations of two coordinates in the cylindrical system r, θ, z. The first subdivision deals with variations in a plane containing the neutral axis. Points may be taken on any straight line in this plane. Other simple geometric arrangements are on triangles, rectangles, or circles in a plane of constant θ. Similarly, variation can be confined to a plane that is perpendicular to the neutral axis (plane of constant z). Subdivisions are based on various simple geometric arrangements. The third division of Class II is obtained by using a circular cylinder (of constant chroma or r). Various harmonies can be obtained by considering two or more points arranged in definite ways on the cylindrical surface.

In Class III, coordinates of color points are varied in three dimensions. Starting with a harmony in a plane of constant θ, one can obtain more interesting harmonies by adding similar color arrangements in another plane. A convenient way of studying such harmonies is to consider several planes containing the neutral axis rather than to attempt to picture the arrangement in 3-space. A second method is with reference to planes of constant z, while a third is based on cylinders of constant r.

TABLE V. Class I. Harmonies in one variable.

1A. Variable z, achromatic harmonies
(*a*) Two color-points
(1) Harmony of analogy. Difference in z is between 4 and 12 ($\frac{1}{2}$ to $1\frac{1}{2}$ Munsell value steps).
Example: *N* 7, *N* 8.
(2) Harmony of contrast. Difference in z is between 20 and 80 ($2\frac{1}{2}$ to 10 Munsell value steps).
Examples: *N* 3, *N* 6; *N* 2, *N* 6; *N* 1, *N* 9.
(*b*) Three points
(1) Small equal steps. Difference in z is between 4 and 12.
Example: *N* 4, *N* 5, *N* 6.
(2) Large equal steps. Difference in z is between 20 and 80.
Example: *N* 2, *N* 5, *N* 8.
(3) Large and small steps.
Examples: *N* 2, *N* 3, *N* 7; *N* 3, *N* 7, *N* 8.
(*c*) More than three points
An obvious extension of the classification for three colors.

TABLE VI. Class I. Harmonies in one variable.

1B. Variable z, chromatic harmonies
(*a*) Two points
(1) Harmony of analogy
Examples: *R* 6/8, 5/8; *B* 6/6, 7/6.
(2) Harmony of contrast
Examples: *P* 6/8, 3/8; *RP* 8/6, 3/6.
(*b*) Three points
(1) Small steps
Examples: *GY* 7/8, 6/8, 5/8; *Y* 8/6, 7/6, 6/6.
(2) Large steps
Example: *R* 8/4, 5/4, 2/4.
(3) Large and small steps
Examples: *BG* 7/4, 6/4, 3/4; *YR* 8/4, 4/4, 3/4.
(*c*) More than three color-points

The foregoing classification is more comprehensive than previous systems of color harmony. It includes as special cases the harmonies mentioned by Chevreul, Munsell, Ostwald, and Birren; and it gives besides a great variety of new harmonies, all expressed in a scientific nomenclature. The system is by no means closed, however. Other geometric arrangements are possible, though most of them will be more complicated and probably less easy to recognize than those considered in Table IV.

6. HARMONIES IN ONE VARIABLE

Harmonies with variable z can be divided into achromatic harmonies and chromatic harmonies (Table V). Under achromatic harmonies are classed (*a*) two-color harmonies, (*b*) three-color harmonies, and (*c*) harmonies with more than three colors. With only two colors, represented by two points on the neutral axis, there are only two possibilities: harmony of analogy and harmony of contrast. According to Tables I and II, a harmony of analogy in z is obtained when the separation of the points is between 4 and 12 units in ω space, which corresponds approximately to a range of $\frac{1}{2}$ to $1\frac{1}{2}$ Munsell value steps. Thus any two grays differing by one Munsell value step exhibit harmony of analogy. For contrast, the difference must be between 20 and 80 units in ω space, corresponding roughly to a range of $2\frac{1}{2}$ to 10 Munsell value steps. Therefore grays differing by $2\frac{1}{2}$ or more Munsell steps show harmony of contrast. The

TABLE VII. Class I. Harmonies in one variable.

2. Variable r
(*a*) Two points
(1) Harmony of analogy
Examples: *N* 7, *R* 7/4; *YR* 4/4, *YR* 4/8.
(2) Harmony of contrast
Examples: *GY* 7/2, *GY* 7/10; *N* 4, *P* 4/12.
(*b*) Three points
(1) Small steps
Examples: *RP* 4/4, 4/8, 4/12; *PB* 5/2, 5/6, 5/10.
(2) Large steps
Example: *N* 4, *R* 4/7, *R* 4/14.
(3) Large and small steps
Example: *N* 8, *Y* 8/8, *Y* 8/12.
(*c*) More than three points

TABLE VIII. Class I. Harmonies in one variable.

3. Variable θ
(*a*) Two points
(1) Harmony of analogy
Examples: *Y* 8/8, *YR* 8/8; 10 *RP* 4/10, 10 *P* 4/10; *YR* 6/6, *Y* 6/6.
(2) Harmony of contrast
Examples: 5 *R* 7/8, 10 *GY* 7/8; 5 *B* 5/6, 10 *R* 5/6.
(*b*) Three points
(1) Small steps
Examples: *RP* 3/10, *P* 3/10, *PB* 3/10.
(2) Large steps
Example: *G* 7/2, *YR* 7/2, *P* 7/2.
(3) Large and small steps
Example: *GY* 6/6, *G* 6/6, *P* 6/6.
(*c*) More than three points

same limits are used throughout the paper for variations of value only.

For three points, (*b*) of Table IV, there are three simple possibilities. The steps may both be small, where "small" indicates a difference in z of between 4 and 12. Or they may both be large, corresponding to a difference in z of 20 to 80. A third possibility is the use of unequal spacing with one small and one large step. An example of this arrangement is obtained from grays having the Munsell notations, *N* 2, *N* 3, and *N* 7.

Obviously there is no need to limit the numbers of colors in an achromatic harmony to three. Four equally spaced points can be used, for example, or n points can be spaced in a regular manner.

The next class of harmonies is listed in Table VI and its classification is similar to that of Table V. First come the harmonies of two colors, represented by two points on a line parallel to the neutral axis. The possibilities are harmonies of analogy such as *R* 6/8, *R* 5/8, and harmonies of contrast such as *P* 6/8, *P* 3/8. Three colors are spaced on a vertical line in the same way as were the grays. An example of 3-color harmony with small steps is *GY* 7/8, 6/8, 5/8; while a harmony with large steps is represented by *R* 8/4, 5/4, 2/4. Large and small steps can be used in combination as in Table V, and larger numbers of colors can be handled in a similar manner.

Table VII indicates the harmonies obtained by varying the radius r, with θ and z constant. These harmonies are unusual arrangements and are difficult to understand at first. They do constitute legitimate harmonies, however, and are suitable for some purposes. The subdivisions are similar to those in Tables V and VI. With two colors, harmony of analogy is now obtained by spacing the colors from 3 to 5 units apart in ω space (or 3 to 5 units of chroma). Harmony of contrast is obtained by using a step of 7 or more units. An example of the former harmony is *YR* 4/4, *YR* 4/8, while an example of the latter is *GY* 7/2, *GY* 7/10.

For three points, small chroma steps yield harmonies such as *RP* 4/4, 4/8, 4/12. Large steps can be used or the combination of large and small steps. More than three colors are handled in a similar manner.

Table VIII covers the final division of the harmonies in one variable. The variable is now θ, and the value and chroma are kept constant. Like the harmonies with variable chroma, the harmonies of variable hue appear somewhat flat,

TABLE IX. Class II. Harmonies in two variables.

1*A*. In a plane of constant θ, points on a straight line
(*a*) Two points
(1) Harmony of analogy
Examples: (positive slope) *BG* 5/6, *BG* 4/4.
(negative slope) *GY* 6/6, *GY* 5/8.
(2) Harmony of contrast
Examples: (positive slope) *YR* 5/6, *YR* 2/2.
(negative slope) *GY* 7/4, *GY* 5/10.
(*b*) Three points
(1) Small steps
Examples: (positive slope) *G* 5/2, 6/4, 7/6.
(negative slope) *P* 6/8, 5/10, 4/12.
(2) Large steps
Examples: (positive slope) *R* 7/6, *R* 4/4, *R* 1/2.
(negative slope) *RP* 8/2, 5/6, 2/10.
(3) Large and small steps
Examples: (positive slope) *GY* 5/2, 7/8, 8/10.
(negative slope) *PB* 7/4, 6/6, 4/10.
(*c*) More than three points

probably because we are accustomed to harmonies in which there is variation of brightness. The subdivisions are similar to those of the previous table. For similarity, the angular separation between two colors lies between $\pm 25°$ and $\pm 43°$, corresponding to a difference of from ± 7 to ± 12 Munsell hue steps. For contrast the separation lies between $\pm 100°$ and $\pm 180°$, or ± 28 to ± 50 Munsell steps. An example of harmony of analogy is *Y* 8/8, *YR* 8/8; and a harmony of contrast is 5 *R* 7/8, 10 *YG* 7/8. Three or more points are handled by obvious extensions of the harmonies of two colors.

This completes the harmonies in one variable. Such harmonies are the simplest ones; but as might be expected, they are generally not the most interesting. Also they are not equally pleasing. All have elements of order and are therefore somewhat harmonious according to our postulates, but this by no means indicates that the degree of harmony is equal in the various cases.

7. HARMONIES IN TWO VARIABLES

If two coordinates are allowed to vary simultaneously, other harmonies result. Table IX lists harmonies in a plane of constant θ, where the color points are allowed to vary on straight lines. Figure 4 was used in obtaining the examples. For two colors, the usual separation into harmonies of analogy and harmonies of contrast applies. It is now possible, however, to use either positive slope or negative slope for the line, and these two possibilities give quite different effects. A harmony of analogy with positive slope is *BG* 5/6, *BG* 4/4. In this arrangement the lighter color is of higher chroma. A distinctly different effect is obtained with negative slope, for example, *GY* 6/6, *GY* 5/8, where the lighter color has the lower chroma. Harmonies of contrast are obtained in a similar manner. Three-color harmonies are classified as usual with small steps, large steps, and a combination of the two. Any number of points can be arranged in a regular manner on a straight line which may have any slope, either positive or negative. The harmonies of Table IX form a varied and interesting class, even though only one hue is employed in any given harmony.

Table X indicates another way of arranging points in a constant-hue plane. Three points may be arranged at the vertices of an isosceles triangle. Under (*a*) are considered the harmonies obtained when the base of the isosceles triangle is horizontal. This means that two of the colors will have the same value but different chromas, while the third color will have a different value and a chroma midway between the other two. If all sides constitute small steps, one obtains an effect of similarity such as found in the example *R* 5/6, 4/4, 4/8. If all sides constitute large steps, a more contrasty effect is obtained. The third possibility is to combine a small change in chroma with a large change in value, as in *YR* 7/4, 4/2, 4/6.

The second division of Table X lists the possibilities for isosceles triangles with vertical bases. This means that two of the colors have the same chroma but different values, while the

TABLE X. Class II. Harmonies in two variables.

1*B*. In a plane of constant θ, triangles
(*a*) Isosceles triangle, horizontal base (s=const.)
(1) All sides constituting small steps Example: *R* 5/6, 4/4, 4/8.
(2) All sides large Example: *PB* 7/6, 4/2, 4/10.
(3) Equal sides large, third side small Example: *YR* 7/4, 4/2, 4/6.
(*b*) Isosceles triangle, vertical base (r=const.)
(1) All sides small Example: *N* 5.5, *G* 6/2, *G* 5/2.
(2) All sides large Example: *RP* 5/2, 2/4, 8/4.
(3) Equal sides large, third side small Example: *N* 4.5, *BG* 5/8, *BG* 4/8.
(*c*) Right triangles
(1) Two mutually perpendicular sides constituting small steps Example: *BG* 6/6, 5/4, 5/6.
(2) Two sides large Example: *Y* 8/4, 8/12, 5/4.
(3) One large and one small side Example: *B* 7/2, 7/6, 3/6.
(*d*) More than three points arranged on a triangle

TABLE XI. Class II. Harmonies in two variables.

1*C*. In a plane of constant θ, rectangles
(*a*) All sides constituting small steps Example: *YR* 7/6, 7/10, 6/6, 6/10.
(*b*) All sides constituting large steps Example: *N* 6, *B* 6/8, *N* 3, *B* 3/8.
(*c*) Large and small sides Example: *B* 7/2, 7/6, 4/2, 4/6.
1*D*. In a plane of constant θ, any number of points spaced on a circle Example: *R* 6/6, 4/2, 4/10, 2/6.

TABLE XII. Class II. Harmonies in two variables.

2. In a plane of constant z
(*a*) Two points Example: *RP* 7/4, *R* 7/8.
(*b*) Three points on isosceles triangle with a vertex on the neutral axis Example: *N* 7, *BG* 7/4, *G* 7/4.
(*c*) Five points at the vertices of two triangles of the type considered in (*b*) Example: *G* 5/4, *BG* 5/4, *N* 5, *RP* 5/4, *R* 5/4.
(*d*) n points spaced on a circle whose center is on the neutral axis Example: *YR* 6/6, *RP* 6/6, *PB* 6/6, *BG* 6/6, *GY* 6/6.
(*e*) n points spaced on a circle whose center is at a chromatic point Example: *R* 5/6, *P* 5/4, *BG* 5/2, *Y* 5/4.

TABLE XIII. Class II. Harmonies in two variables.

3. In a cylinder of constant r
(*a*) Two points (1) Small steps in θ and z Example: *GY* 7/6, *G* 6/6. (2) Large steps in θ and z Example: *G* 3/2, *P* 7/2. (3) Small step in θ and large step in z Example: *R* 7/8, *RP* 3/8. (4) Large step in θ and small step in z Example: *YR* 7/4, *BG* 6/4.
(*b*) n points on an ellipse whose center is on the neutral axis Three points, Example: *R* 2/4, *G* 7/4, *B* 7/4. Four points, Example: *GY* 8/6, *R* 4/6, *PB* 4/6, *P* 2/6.

third has a different chroma and a value midway between the other two. The subdivisions of (*b*) are similar to those of (*a*).

The third division of Table X deals with right triangles. Obviously, this is an orderly arrangement, since two of the colors have constant value and two have constant chroma. The right angle can be placed in various positions, and the perpendicular sides can constitute either small steps or large steps. Also, one of these sides may be large and one small as in *B* 7/2, 7/6, 3/6. Under (*d*) is mentioned the possibility of using more than three points, spaced in an orderly manner along the sides of a triangle.

Table XI contains a list of further harmonies of constant hue. Four points can be arranged at the vertices of a rectangle. Elements of order are obtained by orienting the rectangle with sides parallel and perpendicular to the neutral axis. In each rectangle there are two pairs of points on constant value lines and there are also two pairs on constant chroma lines. Again all sides may constitute small steps, all may be large, or two sides may be large and two small as in the harmony *B* 7/2, 7/6, 4/2, 4/6.

Under 1*D* are mentioned harmonies obtained by using any number of points arranged on a circle. The simplest arrangement would be with these points uniformly spaced. An example with four points is *R* 6/6, 4/2, 4/10, 2/6. There is no *a priori* reason why one need stop with geometrical arrangements on circles. Ellipses and parabolas might also be interesting but they will not be considered here.

Table XII gives the classification of harmonies in two variables in a plane of constant value. In the previous table, the coordinate system was rectangular, but here one has a polar coordinate system. This fundamental difference representing the periodicity of hue alters the form of classification and gives Table XII a different appearance from that of its predecessors. One might think that the limits of allowable and ambiguous regions would be a function of both θ and r, just as these limits are functions of z and r in the plane of constant θ. But an investigation indicated that the hue limits are essentially independent of r. The hue can be distinguished at all chromas, and the hue limits for similarity and contrast remain essentially the same under all circumstances. Thus the limits of Tables I and II are retained without modification.

The remaining division of harmonies in two variables is concerned with cylinders of constant chroma. A definite cylinder is chosen and variation is made in θ and z (hue and value). Table XIII lists the harmonies of this kind, the limits being taken from Tables I and II. Two-color and three-color harmonies are classified in a manner similar to that used on Table XII. The three-color harmonies are obtained conveniently by considering a plane that intersects the circular cylinder. For the special case of intersection at right angles, one obtains circles of constant chroma and value which were considered in Table VIII. With a tilted plane one obtains the more interesting three-color harmonies of Table XIII. The curves of constant chroma are now ellipses and any number of points can be arranged in an orderly manner on a given ellipse. An example of this kind using three points is *R* 2/4, *G* 7/4, *B* 7/4. Another interesting harmony using four colors is *GY* 8/6, *R* 4/6, *PB* 4/6,

P 2/6. Evidently, a great variety of effects is possible with this kind of harmony, since the tilt of the intersecting plane can be altered, as well as the radius of the cylinder and the spacing of the points. Harmonies ranging from the most subdued to the most striking are obtainable by changing these variables.

8. HARMONIES IN THREE VARIABLES

Table XIV indicates some of the possible harmonies obtained when all three coordinates are varied simultaneously. Obviously, this is the most general class of color harmonies and includes a great variety of combinations. It is convenient to consider first harmonies with reference to planes of constant hue. These harmonies are built upon the basis of the two-variable harmonies of Table IX. A plane of constant hue is selected and any number of points are arranged in it according to one of the schemes of Table IX. The designer then selects another plane of closely related hue. In this plane he picks a point having the same value and chroma as one of the points in the original plane. An example is *P* 6/8, *P* 3/8, *RP* 6/8. In (*b*) a similar procedure is used except that the second plane is of a hue which contrasts with the original hue. An extension of this method uses more than one point in the second plane. For example *P* 6/8, *P* 3/8, *B* 6/8, *B* 3/8. Also one need not limit himself to two planes but may use related points in any number of planes of constant hue. An example is *N* 4, *R* 7/6, *R* 6/4, *B* 7/6, *G* 7/6.

Another way of finding these more complicated harmonies is with reference to planes of constant z. Any number of points can be arranged in a plane of constant value according to the methods of Table XII. A parallel plane is now considered and a point is selected having the same r and θ as one of the original points. An example is *N* 6, *R* 6/4, *BG* 6/4, *BG* 5/4. Other effects are obtainable in a similar manner, as indicated in the table under 2(*a*), (*b*), (*c*), and (*d*).

A third method is with reference to cylinders of constant r. The classifications are similar to the previous ones. Finally, it is sometimes convenient to consider planes making an angle with the neutral axis. A harmony is arranged on one of these planes in a manner similar to that used in a plane of constant value (Table XII). Further variety can then be introduced if desired by adding a similar arrangement of points in a parallel plane.

These general harmonies of Table XIV can be based therefore on the simpler harmonies of the previous tables, and they are generally more varied and interesting than the simpler ones. Obviously there are many other orderly arrangements of points in ω space and there is an almost unlimited possibility in building up

TABLE XIV. Class III. Harmonies in three variables.

1. With reference to planes of constant θ
   - (*a*) n points in a plane of constant θ, one related point in another plane, difference in θ is a small step.
     Example: *P* 6/8, *P* 3/8, *RP* 6/8.
   - (*b*) n points in a plane of constant θ, one related point in another plane, difference in θ is a large step.
     Examples: *R* 8/4, 5/4, 2/4, *BG* 5/4;
     BG 7/4, 6/4, 3/4, *R* 7/4.
   - (*c*) n points in a plane of constant θ, similar arrangement of points in another plane.
     Examples: *P* 6/8, *P* 3/8, *B* 6/8, *B* 3/8;
     Y 7/4, *Y* 6/2, *N* 5, *PB* 4/2, *PB* 3/4.
   - (*d*) n points in a plane of constant θ, one point or similar arrangement of points in two or more other planes.
     Example: *N* 4, *R* 7/6, *R* 6/4, *B* 7/6, *G* 7/6.

2. With reference to planes of constant z
   - (*a*) n points in one plane, one related point in another plane, difference in z is a small step.
     Example: *N* 6, *R* 6/4, *BG* 6/4, *BG* 5/4.
   - (*b*) n points in one plane, one related point in another plane, difference in z is a large step.
     Example: *RP* 7/4, *R* 7/8, *R* 3/8.
   - (*c*) n points in one plane, similar arrangement of points in another plane.
     Example: *BG* 6/2, *R* 6/10, *BG* 2/2, *R* 2/10.
   - (*d*) n points in one plane, one point or similar arrangement of points in two or more other planes.
     Example: *RP* 3/2, *R* 3/10, *RP* 7/2, *RP* 6/2.

3. With reference to cylinders of constant r
   - (*a*) n points on one cylinder, one related point on another cylinder, difference in r is a small step.
     Example: *GY* 8/6, *R* 4/6, *PB* 4/6, *P* 2/6, *R* 4/10.
   - (*b*) n points on one cylinder, one related point on another cylinder, difference in r is a large step.
     Example: *N* 5.5, *B* 6/4, *R* 5/4, *R* 5/12.
   - (*c*) n points on one cylinder, similar arrangement of points on another cylinder.
     Example: *G* 3/2, *P* 7/2, *G* 3/6, *P* 7/6.
   - (*d*) n points on one cylinder, one point or similar arrangement of points on two or more other cylinders.
     Example: *R* 7/8, *RP* 3/8, *R* 7/4, *N* 7.

4. With reference to tilted planes
   - (*a*) n points on an ellipse with center on the neutral axis, plus neutral point in the same plane.
     Examples: *N* 5.5, *G* 5/4, *BG* 6/4;
     N 5, *GY* 2/2, *PB* 8/2;
     N 4.5, *P* 6/8, *PB* 3/8.
   - (*b*) n points on an ellipse whose center is at a chromatic point.
     Example: *P* 3/10, *PB* 4/8, *RP* 4/8, *GY* 7/4.

harmonies with color points on space curves and geometric surfaces.

9. EXAMPLES

There are many ways in which the harmonies of this paper can be visualized. Colored lights can be used; or designs can be painted, the various colored areas being standardized spectrophotometrically or by comparison with the *Munsell Book of Color*. Probably the simplest way, however, is to use standardized colored papers. Munsell samples are available in various sizes. If small pieces are adequate, the Munsell Student Set, consisting of chips for 10 constant-hue charts, will be found convenient. *Allcolor papers* are available in $9\frac{1}{2}''\times14''$ sheets at moderate cost. While these papers are not as accurately standardized as the Munsell, they are sufficiently precise for the present purpose.

The appearance of most of the examples listed in Tables V to XIV was investigated by means of color chips mounted on a neutral background of Munsell value 5. Some of the harmonies were also made up in $6''\times8''$ designs of more complicated type. Because of the cost of colored reproductions, however, only gray examples are shown in this paper.

FIG. 5. A two-color achromatic harmony of contrast. Equal areas of $N3$ and $N6$.

Figure 5 exhibits an achromatic harmony of contrast. The areas of the two colors are approximately equal and the colors are $N3$ and $N6$. Figures 6 and 7 are examples of three-color achromatic harmonies. The areas are again approximately equal for the three colors. In Fig. 6 all steps are small, the colors being $N4$, $N5$, and $N6$. In Fig. 7, the steps are large ($N1$, $N5$, and $N9$) giving a harmony of contrast.

10. CONCLUSIONS

The paper presents a scientific development of the classical theories of color harmony. The qualitative ideas of artists and color specialists have been incorporated into a quantitative system depending on the C.I.E. color specification and its transformation into a metric color-space. The entire theory is based on two postulates: pleasing intervals and ambiguous intervals exist between colors, and an orderly geometric arrangement of colorpoints leads to harmony. On this foundation is built a classification of harmonies and these harmonies are tabulated in some detail. The combinations are by no means equally pleasing, but elements of order can be discerned in all of them.

The division into regions of similarity, ambiguity, contrast, and glare is in accordance with classical color harmony. But the numerical designations of these regions are new and are based on preliminary experiments. Similarly, geometric paths through the color solid have been employed by many artists and art teachers —notably by Munsell, Ostwald, Birren, and Graves—but the previous work has lacked definiteness and has not been related to the C.I.E. system of color specification. The numerical limits presented in this paper were determined with a small number of observers and are to be considered as tentative values which could probably be improved by a more extensive research. Indeed, the quantitative extension of the whole subject of color harmony offers many interesting possibilities.

The advantage of the method is that it gives

FIG. 6. A three-color achromatic harmony of analogy. Equal areas of $N\,4$, $N\,5$, and $N\,6$.

FIG. 7. A three-color achromatic harmony of contrast. Equal areas of $N\,1$, $N\,5$, and $N\,9$.

the designer a wealth of new harmonies from which he can select the particular one best fitted to his needs. As with any other scientific aid to the artist, a theory of color harmony can never replace artistic genius, and it makes no such claim. It is merely a tool by which the artist can obtain the desired effect more directly.

Classical color harmony is confined to relations among colors, irrespective of area. In this paper we have simplified conditions to agree with classical theory. Areas are always kept equal, adaptation is fixed at a neutral gray of Munsell value 5, and no attempt is made to compare the various harmonies aesthetically. These limitations will be eliminated in subsequent papers.

In conclusion, we are pleased to acknowledge the helpful suggestions and constructive criticism of Blanche R. Bellamy, Faber Birren, Milton E. Bond, H. W. Gardner, D. B. Judd, and Dorothy Nickerson.

Spectrographic Steel Standards

THE National Bureau of Standards is prepared to furnish a number of steels in rod form suitable for spectrographic standards. The 18 standards now available were selected for checking important representative points of composition among several types of carbon and low alloy steels. The values of concentrations are sufficiently well distributed in most cases to provide analytical curves for Mn, Si, Cu, Ni, Cr, V, and Mo.

The standards are issued in two sizes: (1) cylindrical rod 7/32″ diameter, 4″ long (approximately 22 g); and (2) cylindrical rod 1/2″ diameter, 2″ long (approximately 50 g). The standards are numbered in consecutive order in two series, the first beginning with 401 for the 7/32″ rods and the second beginning with 801 for the 1/2″ rods. The standards may be ordered by number from the National Bureau of Standards, Washington, D. C. at a price of $3.00 per sample, in either series, irrespective of the number of samples ordered. The identifications and compositions of the standards are given in the provisional certificate, which is reproduced below.

U. S. Department of Commerce, National Bureau of Standards, Washington, D. C.
Provisional certificate of analyses of spectrographic steel standards.*

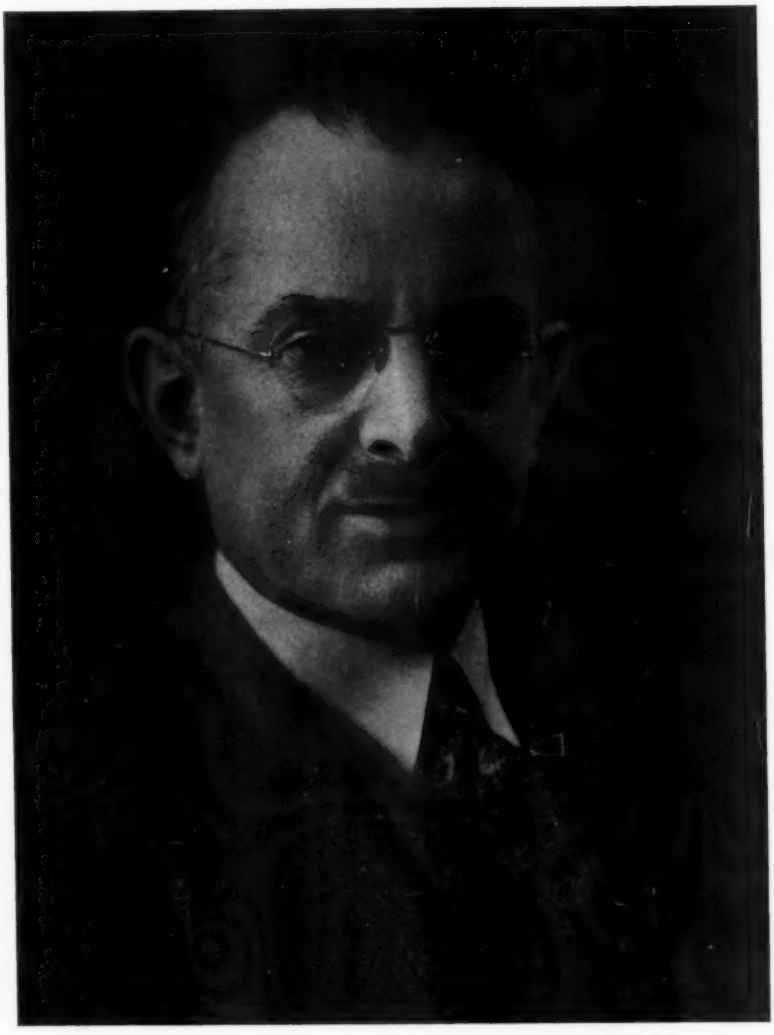
Standards[a]	Name	Mn	Si	Cu	Ni	Cr	V	Mo	
401, 801	B.O.H., 0.4 C[b]	0.34	0.015	—[c]	0.005	0.015	—	—	—
402, 802	B.O.H., 0.8 C	0.46	0.060	0.025	0.010	0.025	—	—	—
403, 803	A.O.H., 0.4 C	0.89	0.25	0.16[d]	0.23	0.28	0.045	0.060	—
404, 804	Basic Electric	—	0.35	0.21	—	0.043	—	0.006	—
405, 805	Medium Manganese	1.38	0.19	0.12	0.15	0.18	0.010	0.010[d]	—
406, 806	Chromium-Vanadium	0.71	0.24	0.10	0.080	0.97	0.23	0.005	—
407, 807	Chromium-Vanadium	0.79	0.29	0.090	0.15	1.15	0.19	0.035	—
408, 808	Chromium-Nickel	0.62	0.22	0.12	1.21	0.64	—	—	—
409, 809	Nickel	0.45	0.13	0.080	3.24	0.20	—	—	—
410, 810	2 Cr—1 Mo	0.38	0.30	0.11	0.13	2.30	0.004[d]	0.97	—
411, 811	Cr-Mo (SAE X4130)	0.65	0.14	0.065	0.29	0.91	0.003	0.15	—
412, 812	Cr-Mo (SAE 4130)	0.60	0.22	—	—	0.66	—	0.20	—
413, 813	A.O.H., 0.4 C	0.67	0.22	0.25	0.18	0.055	0.007	0.006	—
414, —[e]	Cr-Mo (SAE 4140)	0.67	0.26	0.11	0.080	0.99	0.003	0.32	—
415, 815	Bessemer, 0.4 C	1.12	0.093	—	0.010	0.010	0.007	—	—
416, 816	Cr-Mo-Al (Nitralloy G)	0.48	0.25	0.14	—	1.27	0.003	0.16	1.06
417, 817	A.O.H., 0.4 C	0.64	0.18	—	0.105	0.028	0.004	—	—
418, 818	Cr-Mo (SAE X4130)	0.52	0.28	—	0.11	0.96	—	0.22	—

* This supersedes the certificate dated March 24, 1943.
[a] Standards in the 400 series are rods 7/32″ in diameter, 4″ long; and standards in the 800 series are rods ½″ in diameter, 2″ long.
[b] The carbon contents of the 18 steels lie between 0.1 and 0.8 percent.
[c] Dashes in the table indicate elements not certified for spectrographic analysis.
[d] New values.
[e] This standard is not available in the ½″ size.

The Frederic Ives Medal for 1943

Awarded by The Optical Society of America to Loyd Ancile Jones,
Chief Physicist of the Kodak Research Laboratories of the Eastman Kodak Company,
for distinguished work in optics.

This medal, awarded biennially, was endowed in 1928 in honor of Frederic Ives, distinguished for his pioneer contributions to color photography, photoengraving, three-color process printing, and other branches of applied optics.



Dr. Loyd A. Jones